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Hyperfiltration for Renovation of Composite Waste Water at Eight Textile Finishing Plants

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16. ABSTRACT

The report gives results of field evaluations of hyperfiltration at eight plants as a way to renovate composite wastewaters from textile finishing plants. The evaluations included performance assessment of different types of commercially available membranes, reuse of both renovated water and waste concentrates, and the treatability of wastewater concentrates by conventional means. On-site field tests involved a mobile hyperfiltration laboratory. Both cellulose acetate and dynamic membranes, when used with the manufacturers' recommended pretreatment, proved feasible for wastewater renovation. When 90% of the feed was recovered, the renovated water was satisfactory for reuse in scouring, bleaching, dyeing, and finishing. Successful reuse of the residual concentrates, 10% of the feed, containing significant quantities of dyes and chemicals, was not generally demonstrated. However, treatability of the residual concentrate by conventional waste treatment processes produced effluent equivalent in quality to current composite plant discharges. Preliminary operating costs are projected for full-scale systems utilizing cellulose acetate membranes to treat composite wastewater. Savings may be possible from recycled process water, recovery of chemicals and dyestuffs, and use of recycled water at, or near, operating temperature (instead of lower temperature fresh water).

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Waste Water	Membranes	Stationary Sources		11G
Treatment	Cellulose Acetate	Hyperfiltration	14B	11I
Textile Industry	Scouring	Dynamic Membranes	11E	
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ABSTRACT

This research program was conducted to evaluate hyperfiltration for the renovation of composite wastewater at selected textile plants. Eight plants were selected to include several EPA guideline categories. The primary objective was to assess the feasibility of utilizing hyperfiltration as a general treatment method for the textile industry. The assessment required results of membrane performance evaluations conducted in the field, reuse evaluations by textile plant operators, and evaluations of the treatability of the wastewater concentrates by conventional means.

The program was conducted in two phases. Initially, as a screening test phase, samples of the wastewater from twelve plants were transported to Clemson University for processing by hyperfiltration. Reuse was evaluated by the central dye laboratory of a cooperating textile corporation. Results indicated no preferences among the twelve plants, so the selection of eight plants for involvement in the on-site evaluations was made on the basis of guideline categories. The on-site testing phase was accomplished with a mobile laboratory.

The results of the membrane performance evaluations indicated the technical feasibility of both cellulose acetate and dynamic membranes for textile wastewater treatment. The quality of renovated product water, after hyperfiltration, was satisfactory for reuse in scouring, bleaching, dyeing, and finishing when 90% of the wastewater was recovered.

The residual concentrate, 10% by volume, contained significant quantities of dyes and chemicals but direct reuse was not generally demonstrated. The treatability of the residual concentrate by conventional means was, however, established in bench-scale tests as equivalent to that of the current composite plant effluent.

Recycle and the resulting conservation of water, energy (hot water), and chemicals led to the conclusion that hyperfiltration is a very promising technology for wastewater renovation. The chemical removal efficiency suggests hyperfiltration may be useful in the control of toxic emissions. The high-temperature capability of some membranes suggests a major role in energy conservation by direct recycle of that water prior to discharge to the plant drains. Chemical recovery may also be enhanced when process drains are treated individually. However, a major reservation about hyperfiltration remains in the uncertainty of cost because of the lack of a full-scale operating facility.

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SECTION 1

INTRODUCTION

The more stringent requirements for the discharge of industrial wastewater necessitates the evaluation of treatment technologies which provide recycle capabilities. Hyperfiltration[1,2] (reverse osmosis) is a separation technique which yields for textile wastewater a relatively pure product water for recycle and energy conservation when the recycled water is hot. The resulting concentrate, if recycled, effects chemical recovery.

The hyperfiltration process selectively filters soluble and insoluble chemicals from water. This technology has been used successfully in selected industrial applications[3-5] where the recovered chemicals have significant value. The application of hyperfiltration to renovate composite wastewater was demonstrated in a pilot plant at La France Industries.[6] The La France study found that up to 95% by volume of the composite wastewater could be recycled as process water with no effect on dyeing quality. The technical feasibility of recycling the concentrated chemical residue was also determined in a number of full-scale production dyeings. These results were obtained with each of the four basic types of hyperfiltration units listed in Table 1.

The current study investigated hyperfiltration for renovation of composite plant effluent for twelve textile plants. The reuse of 90 - 95% of the composite water, after purification by hyperfiltration, as general plant process water was confirmed by laboratory tests at each mill. The recovery of chemicals from the concentrate would usually require additional study and process modifications. However, the treatability of the concentrate by conventional means was confirmed in bench-scale reactor tests. The results of this study are in agreement with the results from the pilot plant at La France Industries.

Recycle, and the resulting conservation of energy and chemicals, makes hyperfiltration a very promising technology for wastewater renovation. However, a major reservation about hyperfiltration is the cost. While recycle will achieve some savings, the preliminary cost estimates suggest a positive return on capital, there exists no experience with large-scale, long-term operation. In addition to equipment costs, the effect of long-term recycle on plant production quality and costs are also not known. Since the potential of hyperfiltration is very promising, we recommend additional study to establish the economics of plant-scale operations and the effects of recycle on textile production. The additional studies should include process modifications to accomodate recycle and to reduce the liquid effluents from dyeing and finishing processes.

TABLE 1. COMPARISON OF HYPERFILTRATION MODULE CONFIGURATIONS

	Spiral	Tubular	Hollow-fine Fiber	Dynamic
Membrane Material	cellulose acetate	cellulose acetate	polyamide	hydrous Zr(IV) oxide-polyacrylate
Production Rate, m^3/m^2/day	67 - 1000	13 - 200	27 - 2000	200 - 2000
Method of Membrane Replacement	module (on-site)	tubes (on-site)	module (on-site)	in-situ
High Pressure Limitation	membrane compaction	membrane compaction	fiber collapse	no problem
Particulates in Feed	filtration required	no problem	filtration required	no problem
Permissible Feed Range, pH	5.5 - 7.5	5.5 - 7.5	2 - 10	4 - 11
Maximum Temperature, °F (°C)	100 (38)	100 (38)	100 (38)	>195 (>90)

This report summarizes the results obtained in this study under the general categories of textile plant characteristics, wastewater reuse and treatability, membrane performance, and cost estimates. The detailed results and data obtained at each plant are given in the appendices of this report.

PURPOSE AND SCOPE

The purpose of this study was to evaluate hyperfiltration for the renovation of composite wastewater at selected textile plants. The selection was made to include a variety of textile manufacturing processes. Consequently, the selection involved examples of several of the EPA guideline categories.[7] The primary objective of this study was to obtain results that when combined with the results obtained from the La France pilot plant will permit a feasibility assessment of hyperfiltration as a general treatment method for the textile industry. The study involved the measurement of membrane performance with minimum pretreatment, the evaluation of reuse of both the purified product water and the concentrated residue, and the determination of the treatability of the concentrate by conventional means.

Even though pretreatment may be a method to improve the cost effectiveness of membrane systems, it was not in the scope of this study to develop pretreatments, beyond the minimum requirements for pH control, temperature, and coarse filtration (∿25-micron) as specified by the membrane manufacturer. Likewise, it was not within the scope of this study to develop membrane cleaning procedures, even though there is a potential to decrease significantly the costs of membrane systems.

PROGRAM PLAN

This study was conducted by Clemson University for the South Carolina Textile Manufacturers Association and the twelve textile mills who participated in the study (Table 2). The Oak Ridge National Laboratory (ORNL) loaned the mobile hyperfiltration test trailer to Clemson for this study and assisted in its operation and maintenance. ORNL also provided consultation regarding membrane performance. Membrane equipment companies cooperated in this study by providing units for tests and evaluation. The study was partially funded by a grant[8] from the Environmental Protection Agency.

The program plan included a four-month screening test phase. The screening tests (Appendix A) consisted of membrane performance evaluations conducted at Clemson with 0.4 m^3 (100-gallon) samples of wastewater from each mill. No significant differences were detected in membrane performance with any of the composite waste streams. Laboratory-scale tests of recycle were conducted both at the central dyeing laboratory of Deering Milliken Research Corporation and by the laboratory at each mill. The test dyeings all indicated that the renovated water was completely satisfactory as process water even when the recovered fraction was greater than 90% of the original wastewater volume.

The initial program schedule allowed for six plant sites. The program

TABLE 2. PLANTS, FIBERS PROCESSED, AND EFFLUENT GUIDELINE SUBCATEGORIES INVOLVED IN FIELD TESTING

	Fibers Processed			Waste Discharge Subcategory[a]	
Plant[b]	Cotton	Synthetic	Wool	No.	Description
Plant #50	X	X	X	5	Knit fabric finishing
Plant #60		X		6	Carpet mill
Plant #70	X	X	X	7	Stock and yarn dyeing
Plant #40	X	X		4	Woven fabric finishing
Plant #80	X	X		8	Commission finishing
Plant #81	X	X		8	Commission finishing
Plant #82	X	X	X	8	Commission finishing
Plant #83	X	X	X	8	Commission finishing
Plant #41	X	X		4	Woven fabric finishing
Plant #42	X	X		4	Woven fabric finishing
Plant #43	X	X	X	4	Woven fabric finishing
Plant #44	X	X		4	Woven fabric finishing

[a] Reference 7.
[b] Code number of individual plant.

was later amended to include two additional plants. The field tests were conducted using the ORNL mobile laboratory operated by Clemson University and plant personnel.

Laboratory-scale evaluations of the reuse of both the purified water and the concentrated chemical residue were conducted at each mill by plant personnel. Because the recycle of the chemical residue is not always immediately practical, Texidyne, Inc. was contracted by SCTMA to evaluate the conventional treatability of the concentrate from six of the plants.

This study began in August, 1974. The screening tests were completed by December, 1974, with initial field testing beginning in January, 1975, after a brief period of equipment modification due to extremely cold weather. The field tests were concluded in October, 1975. Evaluation of the reuse test dyeings and preparation of cost estimates were done during the spring of 1976. Review and discussion of the results with the textile mills was delayed by the energy crisis of 1976 - 1977.

SECTION 2

CONCLUSIONS

The conclusions of this study relating to reuse are:

- The quality of product water, purified by passing through a hyperfiltration membrane, was satisfactory for reuse in scouring, bleaching, dyeing, and finishing.

- The residual concentrate contains significant quantities of dyes and chemicals in a mixture, but will require specific study programs at each individual mill to develop reuse.

The conclusion about the treatability of the concentrate is:

- The treatability of the residual concentrate by conventional means was established in bench-scale tests to be equivalent to the treatment used at each plant for treating the composite plant effluent.

The conclusions of this study relating to membrane performance are:

- The technical feasibility of both cellulose acetate and dynamic membranes, with corresponding pretreatments, to renovate textile wastewater was established.

- Preliminary cost projections for full-scale systems utilizing cellulose acetate membranes to treat the composite wastewater indicate a total cost range of \$1.17 to \$1.47 per 1000 gallons, including pretreatment and amortization.

The preliminary cost projections did not include any credits for recycle. Water supply costs will be reduced if 90% recycle is employed. Energy savings are also possible since the recycle water is significantly warmer than the current supply. Chemical recovery will be realized in some situations.

SECTION 3

RECOMMENDATIONS

Recycle, and the resulting conservation of energy and chemicals, makes hyperfiltration a very promising technology for wastewater renovation. However, a major reservation about hyperfiltration is the cost. While recycle will achieve some savings, and preliminary cost estimates suggest a positive return on capital, there exists no experience with large-scale, long-term operation. In addition to equipment costs, the effect of long-term recycle on plant production quality and costs are also not know. Since the potential of hyperfiltration is very promising, we recommend additional study to establish the economics of plant-scale operations and the effects of recycle on textile production. The additional studies should include process modifications to accommodate recycle and to reduce the liquid effluents from dyeing and finishing processes.

It is strongly recommended that these evaluations be made before irrevocable decisions are required regarding large expenditures of capital to meet the national environmental protection goals of 1983 - 1985.

Since the cost of the membrane modules is a significant factor in the determination of the economic practicality of this technology, the following general recommendations relate to improvements in the equipment performance with textile wastes.

(1) Development of membrane cleaning procedures to periodically restore flux.

(2) Development of physical and chemical pretreatment methods to reduce membrane fouling to increase average flux and to prolong membrane life.

(3) Development of membrane module designs to reduce costs and to minimize horsepower requirements.

(4) Evaluation of the potential for chemical reclamation from the residual concentrate.

SECTION 4

TEXTILE PLANT CHARACTERISTICS

Parameters characterizing the production operation at the eight plants involved with the on-site testing phase of this study are presented in Table 3. The data tabulated are for the period of the on-site testing phase of this study (1975). Obviously, these data do not necessarily reflect the present status of these plants. This information is included solely to assist the reader in judging the applicability of the results and conclusions to a particular situation. In this section the range of parameters involved in this study are presented. The details for each plant are included in the appendices.

In every case, 85 - 95% of the composite wastewater comes from the preparation, dyeing, and finishing unit operations within the plant. The principal materials potentially involved in recycle from composite wastewater renovation are the water, salt, auxiliary chemicals, and dyes. Some energy conservation will be realized when the warm recycle water reduces the need for heating. In the case of high-temperature membranes, significant energy conservation may be realized by direct recycle at, or near, process temperature. An indication of the amount of resources discharged with the wastewater and the corresponding potential savings are given in Table 4. The data indicate that savings may average \$2.63/kgal (69¢/m^3) of water discharged. Of course, the value for individual situations vary widely depending largely on the local costs for water supply, waste treatment, and energy. The cost of achieving the savings will also vary with individual situations.

FIBERS PROCESSED AND CHEMICALS USED

The wet finishing processes generate most of the plant composite wastewater. The unit processes, the fiber mix, and the principal dyes and chemicals employed at the mills are tabulated in Table 5. Both continuous and batch processing methods were included in this study. Cotton, polyester, nylon, and acrylic fibers were the predominant fibers processed. Correspondingly, a wide range of dye types were treated by membranes in the course of this study.

WASTEWATER CHARACTERISTICS

The variety of dyes, auxiliary chemicals, scouring chemicals, and finishes produce complex and variable wastewater compositions. Table 6 presents the wastewater characteristics of the twelve plants in terms of monthly averages of treatment plant influent parameters. This information

TABLE 3. PRODUCTION CAPACITY PARAMETERS

	Plant #50	Plant #60	Plant #70	Plant #40
QUANTITIES USED				
Water (total to plant)				
m^3/day	9,091	2,724	1,892	20,833
(gallons/day)	(2,400,000)	(720,000)	(500,000)	(5,500,000)
Effluent evaluated for reuse during on-site tests	total plant outfall	dyeing operation	total plant outfall	total plant outfall
Dyes				
kg/day	na	na	250	8,182
(pounds/day)	na	na	(550)	(18,000)
Auxiliary Chemicals				
kg/day	na	na	1,140	39,342
(pounds/day)	na	na	(2,514)	(86,750)
Energy (for process steam)				
joules/day	na	na	292×10^9	7358×10^9
(Btu/day)	na	na	(278×10^6)	(7008×10^6)
UNIT COSTS				
Water				
¢/m^3	na	na	6	2
($/1000 gallons)	na	na	(0.23)	(0.06)
Fuel Oil				
¢/10^7 joules	na	na	1.9	2.0
($/$10^6$ Btu)	na	na	(2.06)	(2.20)

TABLE 3. (continued)

	Plant #80	Plant #81	Plant #82	Plant #83
QUANTITIES USED				
Water (total to plant)				
m^3/day	13,257	30,682	6,629	32,197
(gallons/day)	(3,500,000)	(8,100,000)	(1,750,000)	(8,500,000)
Effluent evaluated for reuse during on-site tests	dyehouse only	total plant outfall excluding print shop	total plant outfall	total plant outfall
Dyes				
kg/day	3,162	4,545	537	5,293
(pounds/day)	(6,973)	(10,000)	(1,184)	(11,644)
Auxiliary Chemicals				
kg/day	29,035	7,319	8,224	21,130
(pounds/day)	(64,023)	(16,100)	(18,134)	(46,486)
Energy (for process steam)				
joules/day	4630×10^9	12.8×10^{12}	1327×10^9	8491×10^9
(Btu/day)	(4410×10^6)	(12.1×10^9)	$1264 \times 10^6)$	(8087×10^6)
UNIT COSTS				
Water				
¢/m^3	4	5	-	3
($/1000 gallons)	(0.15)	(0.19)	-	(0.12)
Fuel Oil				
¢/10^7 joules	1.0	1.1	1.5	1.4
($/$10^6$ Btu)	(1.10)	(1.18)	(1.65)	(1.51)

TABLE 4. POTENTIAL CONSERVATION BY RECYCLE FOR THE TEXTILE INDUSTRY

	Water Discharge (10^3 kgal/d)	Materials Used			Process Thermal Energy (10^9 Btu/d)
		Dyes (10^3 #/d)	Auxiliary (10^3 #/d)	Salt (10^3 #/d)	
Study Total[a]	31	60	28[b]	27	38
Industry Total	706[c]	1291	594	581	784[d]
Recycle Potential	635	129	489	481	352[e]
Estimated Annual Savings[f]	$79 x 10^6$	$95 x 10^6$	$24 x 10^6$	$3 x 10^6$	$264 x 10^6$

[a] EPA Grant No. S802973.

[b] Exclusive of 176,000 pounds of NaOH used daily at these plants.

[c] 1972 census of manufacturers, assuming 250 days/year on stream.

[d] Industry estimate of 50 x 10^6 barrels/yr; 70% in wet finishing.

[e] 15 x 10^6 barrels/yr.

[f] Unit costs: water @ $0.5 kgal; dye @ $3/#; auxiliary chemicals @ $0.2/#; salt @ $44/ton; process steam @ $2/10^6$ Btu.

TABLE 5. PROCESS CHARACTERISTICS OF THE MILLS INVOLVED IN ON-SITE TESTS

Plant	Plant #50	Plant #60	Plant #70	Plant #40
Types of Processes	jet dyeing, atmospheric becks	carpet dyeing, atmospheric becks	high-temperature package dyeing machines, atmospheric skein-dyeing equipment	scouring, bleaching, dyeing, and finishing in continuous ranges
Fabrics Processed	polyester 65% rayon 20% wool 15%	acrylic 10% nylon 80% polyester 10%	acrylic 10% nylon 1% wool and mohair 1%	cotton; cotton-polyester blends
Chemicals and Dyes Used	disperse, acid direct dyes	acid, premetallized, disperse dyes	basic dyes	sulfur, vat, fiber reactive, napthol dyes
Plant Classification for the Purpose of Waste Effluent Limitations	Subcategory 5 Knit fabric finishing	Subcategory 6 Carpet mill	Subcategory 7 Stock and yarn dyeing	Subcategory 4 Woven fabric finishing

TABLE 5. (continued)

Plant	Plant #80	Plant #81	Plant #82	Plant #83
Types of Processes	scouring, bleaching, dyeing, finishing in continuous ranges	scouring, bleaching, dyeing, finishing in continuous ranges	scouring, bleaching, dyeing, finishing in continuous ranges	scouring, bleaching, dyeing, finishing in continuous ranges
Fabrics Processed	cotton; cotton-polyester blends	cotton; cotton-polyester blends	cotton; cotton-polyester blends	cotton; cotton-polyester blends
Chemicals and Dyes Used	sulfur, vat fiber reactive, napthol dyes	sulfur, vat fiber reactive, napthol dyes	sulfur, vat fiber reactive, napthol dyes	sulfur, vat fiber reactive, napthol dyes
Plant Classification for the Purpose of Waste Effluent Limitations	Subcategory 8 Woven fabric finishing	Subcategory 8 Woven fabric finishing	Subcategory 8 Woven fabric finishing	Subcategory 8 Woven fabric finishing

TABLE 6. PLANTS, GUIDELINE SUBCATEGORIES, AND EFFLUENT CHARACTERISTICS

		Waste Discharge Characteristics						
	Guideline	Flow		Temperature			COD	TDS
Plant	Subcategory	10^6 GPD	$10^3 m^3/d$	°F	°C	pH	(mg/ℓ)	(mg/ℓ)
#50	5	2.4	9.1	140	60	7.0	450	350
#60	6	0.7	2.7	100	38	4.0	na	430
#70	7	1.0	3.8	130	54	4.0	700	800
#40	4	4.4	16.7	95	35	12.4	1200	3000
#80	8	3.0	11.4	107	42	9.8	1284	na
#81	8	12.0	45.4	120	49	11.0	1780	1750
#82	8	2.0	7.6	91	33	7.3	670	1130
#83	8	8.3	31.4	99	38	11.4	na	1850
#41	4	2.0	7.6	110	43	11.0	2400	3600
#42	4	4.8	18.2	88	31	11.0	890	980
#43	4	6.0	22.7	81	27	11.6	1033	2580
#44	4	1.4	5.3	84	29	11.3	na	na

During the on-site testing, grab samples were taken to characterize the wastewater feed to the membrane units. As an example of these results, Table 7 presents the grab sample results for Plant #40. Complete results of analyses for grab samples taken at each plant are given in the appendices of this report.

TABLE 7. CHEMICAL ANALYSES OF SELECTED WASTEWATER[a] GRAB SAMPLES PLANT #40

SAMPLE NUMBER	633	648	654
DATE TAKEN	4/2/75	4/3/75	4/7/75
PARAMETER[b]			
COD	1360	1520	1860
BOD	270	330	380
TOC	534	620	563
Alkalinity	1549	1424	1158
Hardness	13	15	13
Total Solids	4000	3140	3812
Dissolved Solids	2920	2888	3634
Volatile Solids	768	910	1020
Color	350	250	300
Turbidity	6.0	10	5.5
Conductivity	6400	5800	4500
Phenol	0.004	0.097	0.053
pH	11.7	11.7	11.5
Mercury	0.43	0.43	0.04
Calcium	2.0	2.5	1.5
Iron	0.2	0.2	0.2
Nickel	0.1	0.1	0.1
Chromium	13	0.15	31
Zinc	2.2	1.3	3.2
Copper	0.4	0.2	0.4
Magnesium	1.9	2.0	1.8

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (mg/ℓ SIO_2), conductivity (μmho/cm), pH (unitless), and mercury (μg/ℓ).

SECTION 5

EQUIPMENT AND PROCEDURES

The evaluation of membranes for treatment of textile wastewater was conducted in two phases: a series of laboratory screening tests, and on-site evaluations. Both phases of testing used the mobile hyperfiltration laboratory loaned by ORNL. The screening tests were conducted at Clemson University with 0.4 m^3 (100-gallon) samples of wastewater. The screening tests (Appendix A) were primarily useful in selecting plants for the on-site testing phase.

In both phases of the test program evaluation was made by plant personnel of the potential for reuse of the product water and the concentrate. The particular emphasis of the on-site testing phase was the evaluation of membrane performance over a significant period of operation (approximately 250 hours).

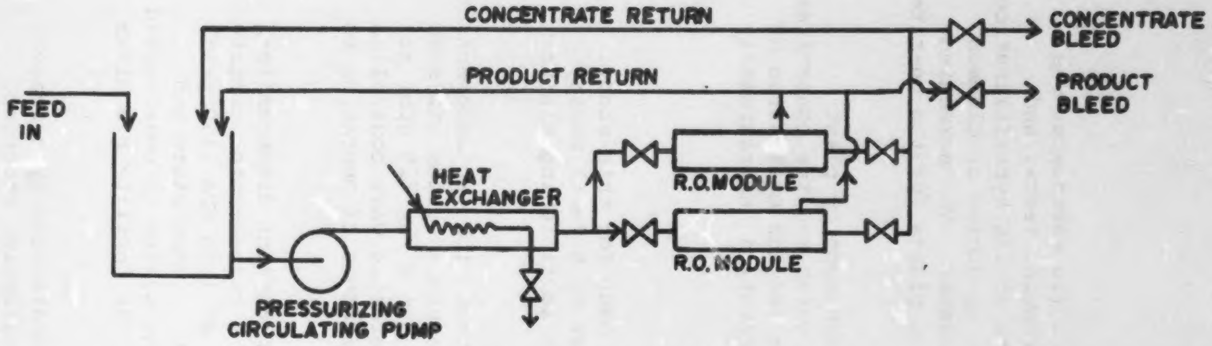
MOBILE LABORATORY

The mobile laboratory was loaned to Clemson by ORNL for this study. The laboratory was housed in a 9.1 m x 2.4 m (30 feet by 8 feet) Dorsey trailer. The laboratory was transported to the textile finishing plants by tractors provided by the host company.

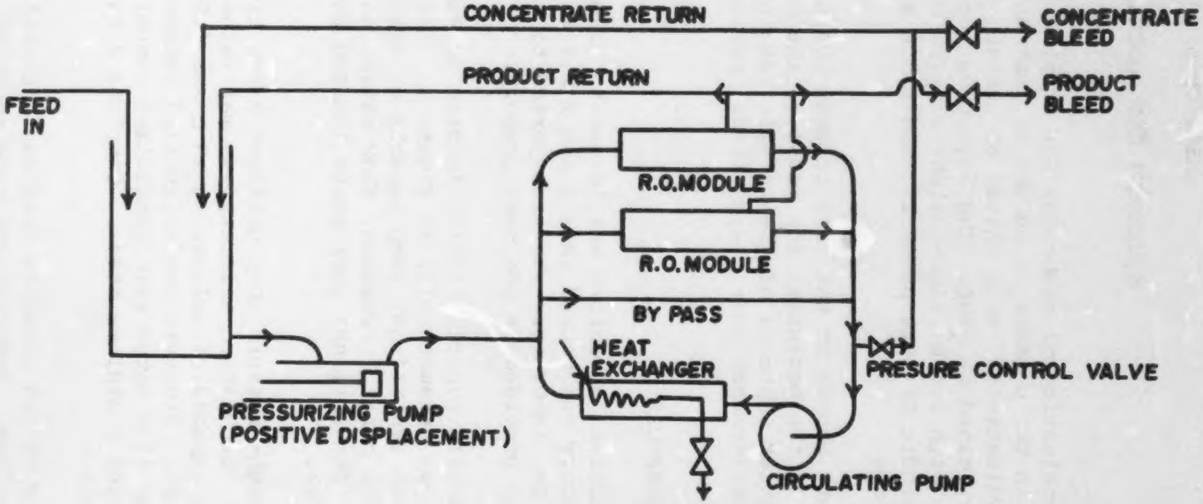
The mobile hyperfiltration laboratory was equipped with two independent systems shown schematically in Figure 1. The low-pressure system utilized a multistage centrifugal pump capable of delivering 3.4 m^3/hr (15 gpm) at 3.4 MPa (500 psig). Pressure, flow rates, and temperature were controlled manually. The internal pump parts limited the temperature of operation to 71°C (160°F).

The high-pressure loop utilized a positive displacement diaphram feed pump. The circulation velocity was maintained with a canned-rotor centrifugal pump capable of delivering 23 m^3/hr (100 gpm) at 1.03 MPa (150 psid) differential. Pressure was controlled automatically. Temperature and circulation flow rates were controlled manually. The system is constructed of 300-series stainless steel. Complete details of the facility are given in Reference 9.

The pH of the incoming feed was controlled automatically by a reagent addition system. Temperatures were recorded on a multipoint recorder. Pressures were indicated by boudon tube gauges and flow rates by rotameters or venturi tubes. Conductivities were measured with a dip-type cell,


CONCENTRATE RETURN
CONCENTRATE BLEED
PRODUCT RETURN
PRODUCT BLEED
FEED IN
HEAT EXCHANGER
R.O.MODULE
R.O.MODULE
PRESSURIZING CIRCULATING PUMP

LOW PRESSURE LOOP


CONCENTRATE RETURN
CONCENTRATE BLEED
PRODUCT RETURN
PRODUCT BLEED
FEED IN
R.O.MODULE
R.O.MODULE
BY PASS
HEAT EXCHANGER
PRESURE CONTROL VALVE
PRESSURIZING PUMP (POSITIVE DISPLACEMENT)
CIRCULATING PUMP

HIGH PRESSURE LOOP

Figure 1. Schematic drawing of hyperfiltration loops in the mobile hyperfiltration laboratory.

optical density by a spectrophotometer, and pH by a dip-type probe. Flow rates for membrane flux measurements were made with a graduated cylinder and clock.

ON-SITE TEST PROCEDURES

The goals of the on-site tests were (1) to obtain samples of renovated composite wastewater for evaluation of reuse, and (2) to obtain engineering data on membrane performance with composite wastewater. Tests were made, when time allowed, with unmixed effluents from unit manufacturing processes within the plant.

The schedule called for a four- or five-week stay at each of the eight mills. The schedule was extended at some sites due to equipment problems and plant holidays. One-half week on arrival and one-half week at departure were devoted to utilities connection and equipment check-out.

Membranes were selected for use at each site based on availability and the waste characteristics. The membranes evaluated are indicated in Table 8. All wastewater was prefiltered through 25-micron cartridge filters before entering the laboratory trailer. The pH was adjusted when necessary to meet module manufacturers specified ranges. A typical equipment arrangement during on-site testing is shown in Figure 2.

To achieve the project objectives, a three-phase on-site testing program was undertaken: (1) reuse test sample generation, (2) 200-hour engineering test of membrane performance, and (3) special tests (when time allowed). During each phase a number of water samples were taken for detailed chemical analyses. Complete details of the procedures followed at each mill are given in the appendices.

TABLE 8. MEMBRANE EVALUATION SCHEDULE

		Membrane Type		
Plant	Test Period	Dynamic Zr-PAA	Spiral-wound Cellulose Acetate	Tubular Cellulose Acetate
Plant #50	12/3/75 - 1/15/75	X	X	X
Plant #60	1/15/75 - 2/26/75	X	X	X
Plant #70	2/26/75 - 3/26/75	X	X	
Plant #40	3/26/75 - 4/23/75	X	X	
Plant #80	4/23/75 - 5/21/75	X	X	
Plant #81	5/21/75 - 6/25/75	X		
Plant #82	6/25/75 - 7/30/75	X	X	
Plant #83	7/30/75 - 9/04/75	X	X	

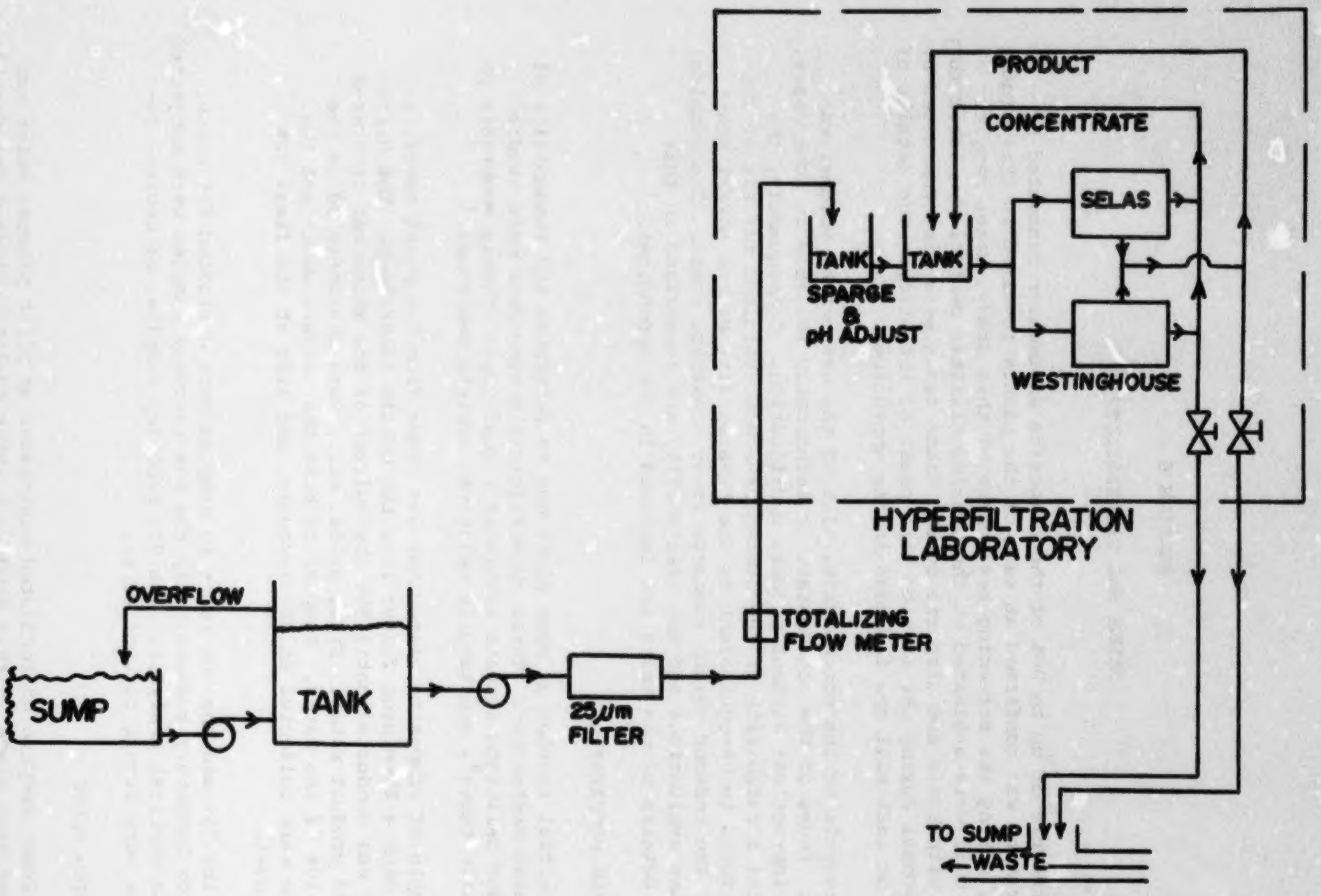

PRODUCT
CONCENTRATE
SELAS
TANK
TANK
SPARGE & pH ADJUST
WESTINGHOUSE
HYPERFILTRATION LABORATORY
OVERFLOW
SUMP
TANK
25 μm FILTER
TOTALIZING FLOW METER
TO SUMP
WASTE

Figure 2. Flow schematic for equipment set-up at Plant #40.

SECTION 6

REUSE AND TREATABILITY

The recycle of up to 90% of the composite wastewater renovated by hyperfiltration was confirmed at each of the plants involved in this study. Initially, during the screening test phase of this study, water samples from each mill were evaluated at the Deering Milliken central dye laboratory for reuse with basic and disperse dyes. Reuse tests were also conducted by plant personnel during the on-site test phase of the study. The details of the tests at each mill are included in the appendices.

The recycle of the concentrate, ∿10% of the wastewater volume, was evaluated. Reuse of the concentrate is technically feasible in some cases, but often impractical without process modification. Consequently, the conventional treatability of the concentrate was evaluated for six of the mills and found to be equivalent to the treatability of the normal plant effluent. The reduced volume suggests lower treatment costs. The results of the reuse evaluations and the treatability are summarized in this section. Details of the tests are included in the appendices.

REUSE SAMPLE PREPARATION

The initial testing at each plant was to determine the reusability of the renovated wastewater. Three hyperfiltration membranes were studied: spiral-wound cellulose acetate membranes[1], dual-layer dynamic membranes on Selas ceramic tubes[2], and tubular cellulose acetate membranes.[3]

A sample of composite wastewater was drawn from the plant sewer, and pumped through a 25-micron filter into the mobile laboratory. The hyperfiltration was conducted until 90% (by volume) of the water was recovered as purified product water. Dyes, salts, etc., were concentrated in the remaining 10% of the water. Samples of both the product water and the concentrate were collected at 75% recovery, and also at the final 90% recovery level.

Both the 75% and the 90% recovery samples were evaluated for reuse. However, for budgetary reasons, only the 90% recovery samples were subjected to detailed chemical analyses. The 90% recovery samples, of course, represent the more severe test of reuse.

PRODUCT WATER REUSE

The direct recycle of renovated wastewater as plant process water was confirmed by each plant in this study. A water quality standard for textile process water is not available. These data do not define chemical analyses limits for reuse either. No test results were reported for reuse of hyperfiltration product water from the treatment of textile wastewater.

The results of chemical analyses of the water evaluated for reuse are tabulated for each membrane type in Tables 9 - 11. In general, the product water contains more dissolved solids, inorganics and organics, than normal tap water but is low in metals. Because membranes do not separate 100% of the dissolved material, the 10% by volume residue is only about eight times as concentrated as the plant composite wastewater (instead of the volumetric factor of 10). The purified product water contains some chemicals, also because the membranes do not reject 100% of the dissolved materials. The samples of purified product water evaluated for reuse were obtained just at the end of the concentration test, and thus contain more chemicals than the average mixed product water would have if it had all been collected. In fact, for the membranes tested the mixed product water from a full-scale hyperfiltration plant would contain only about one-third the contaminant levels of these reuse samples.

Because the question of water recycle is very important in this study brief summaries of the tests conducted by each mill are included here as well as in more detail in the appendices.

Plant #50

The samples were misplaced in transit from the mill site to the corporation central laboratory and hence no reuse evaluations were conducted.

Plant #60

Laboratory dyeings, including tricolor carpet shades, were conducted by the plant laboratory with no significant differences in results obtained with normal tap water.

Plant #70

The product water was evaluated for reuse in a laboratory dyeing using basic dyes. The product water was found to be equivalent to normal process water.

Plant #40

The product water was used in the laboratory with reactive dyes on 100% cotton fabrics. It was also used in a padding formulation containing no dye to determine if any background color would interfere with continuous pad-dry-thermosol-steam operation. No problems were encountered in the test dyeings and the color fastness was the same as obtained with normal plant water.

Plant #80

Laboratory evaluation for continuous range dyeings were run using product water to make up the dyebath. A control run was made using regular

TABLE 9. CHEMICAL ANALYSES OF SPIRAL-WOUND CELLULOSE ACETATE MEMBRANE PRODUCT WATER EVALUATED FOR REUSE

PLANT	#50	#60	#70	#40
% RECOVERY	90%	92%	90%	90%
PARAMETER[a]				
COD	72	64	368	178
BOD	10	5	80	40
TOC	22	13	84	25
Alkalinity	5	10	-50	32
Hardness	1	<1	<0.3	<1
Total Solids	10	10	144	1222
Dissolved Solids	8	10	144	1222
Volatile Solids	4	4	80	122
Color	10	8	10	30
Turbidity	2	2	-	20
Conductivity	44	37	135	1650
Phenol	0.52	-	0.05	0.22
pH	6.7	6.5	4.6	6.4
Mercury	<0.01	<0.01	0.002	<0.001
Manganese	<0.01	0.01	<0.01	<0.1
Calcium	0.46	0.38	<0.01	<0.01
Iron	0.35	0.27	0.57	1.79
Nickel	<0.01	<0.01	<0.1	<0.1
Chromium	<0.1	-	<0.01	<0.1
Zinc	0.10	-	0.01	0.133
Copper	0.1	<0.1	0.17	<0.1
Magnesium	0.14	0.11	2.56	1.77

TABLE 9. (continued)

PLANT	#80	#82	#83
% RECOVERY	90%	90%	90%
PARAMETER[a]			
COD	208	66	53
BOD	105	26	11
TOC	42	14	43
Alkalinity	-52	27	200
Hardness	5	1	10
Total Solids	472	82	74
Dissolved Solids	472	82	74
Volatile Solids	96	38	48
Color	-	-	10
Turbidity	-	-	0.5
Conductivity	830	65	83
Phenol	0.055	0.07	0.14
pH	4.0	6.5	6.0
Mercury	<0.001	<0.001	<0.001
Manganese	0.05	<0.01	<0.01
Calcium	<0.01	<0.01	0.73
Iron	2.68	0.66	<0.01
Nickel	0.41	<0.01	<0.01
Chromium	0.11	0.04	<0.01
Zinc	1.09	0.33	0.16
Copper	0.15	0.03	0.05
Magnesium	2.10	0.04	0.62

[a] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE 10. CHEMICAL ANALYSES OF SELAS DYNAMIC MEMBRANE PRODUCT WATER EVALUATED FOR REUSE

PLANT	#50	#60	#70	#40
% RECOVERY	90%	92%	90%	90%
PARAMETER[a]				
COD	84	120	226	218
BOD	15	2	56	58
TOC	20	28	88	27
Alkalinity	10	19	35	73
Hardness	<1	<1	≤0.3	3
Total Solids	42	62	272	1440
Dissolved Solids	42	62	272	1432
Volatile Solids	4	18	126	140
Color	-	10	-	20
Turbidity	-	-	-	10
Conductivity	66	55	250	2200
Phenol	0.44	0.03	0.06	0.01
pH	7.2	6.8	8.5	7.0
Mercury	<0.01	<0.01	<0.001	<0.001
Manganese	0.01	0.03	<0.01	0.27
Calcium	0.68	0.55	0.01	0.36
Iron	0.40	0.47	0.79	1.76
Nickel	<0.01	<0.01	<0.1	<0.1
Chromium	0.19	-	<0.01	<0.1
Zinc	0.08	-	0.08	0.30
Copper	0.1	<0.1	0.1	0.112
Magnesium	0.18	0.15	1.72	1.97

TABLE 10. (continued)

PLANT	#80	#81	#82	#83
% RECOVERY	90%	90%	90%	90%
PARAMETER[a]				
COD	144	328	94	103
BOD	52	$\geq$105	11	8
TOC	22	-	17	39
Alkalinity	102	72	31	64
Hardness	1	2	2	10
Total Solids	634	500	1140	886
Dissolved Solids	634	500	1135	885
Volatile Solids	254	250	130	76
Color	-	-	5	15
Turbidity	-	-	8	1.0
Conductivity	800	350	1300	1550
Phenol	0.08	0.04	0.015	0.015
pH	9.0	8.6	6.8	6.8
Mercury	<0.001	<0.001	<0.001	<0.001
Manganese	0.13	0.01	<0.01	0.09
Calcium	0.47	0.1	<0.01	0.51
Iron	2.48	0.47	0.17	<0.01
Nickel	0.35	0.20	0.09	<0.01
Chromium	0.11	0.1	<0.01	<0.01
Zinc	0.46	0.07	0.18	0.71
Copper	<0.1	0.1	0.04	0.09
Magnesium	1.57	0.01	0.04	0.71

[a] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE 11. CHEMICAL ANALYSES OF TUBULAR CELLULOSE ACETATE MEMBRANE PRODUCT WATER EVALUATED FOR REUSE

PLANT	#50	#60
% RECOVERY	90%	92%
PARAMETER[a]		
COD	468	284
BOD	24	14
TOC	800	63
Alkalinity	50	5
Hardness	1	3
Total Solids	274	186
Dissolved Solids	267	181
Volatile Solids	144	80
Color	180	40
Turbidity	30	10
Conductivity	270	140
Phenol	0.59	0.03
pH	6.7	5.6
Mercury	<0.01	<0.01
Manganese	0.04	<0.01
Calcium	0.82	0.66
Iron	0.25	0.30
Nickel	<0.01	<0.01
Chromium	0.27	-
Zinc	1.41	-
Copper	0.1	0.1
Magnesium	0.26	0.11

[a] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

plant water on the same fabric style. A critical shade was chosen in disperse/vat, disperse/sulfur, and disperse/reactive combinations. Reuse of product water in the dyebath did not affect the shade. Shade variation was not more than is expected when repeating the same dyeing with regular plant water.

Plant #81

The product water was used in the plant laboratory with disperse/fiber reactive dye mixtures and disperse/vat dye mixtures on 65%/35% polyester/cotton fabric. No problems were encountered in the laboratory test dyeings and the color fastness was the same as obtained with normal plant water.

Plant #82

The product water was used in the laboratory with disperse, acid, and premetallized dyes on polyester/wool blends and 100% textured polyester fabric. The dyeings were conducted in atmospheric pressure becks to simulate plant equipment. No problems were encountered in the test dyeings and the shade obtained was the same as obtained with normal plant water.

Plant #83

Laboratory dyeings using product water and concentrate water were made on 54/45 polyester avril fabric, 100% T-65 polyester fabric, and 100% orlon fabric and multifiber test cloth.

CONCENTRATE REUSE

Samples of concentrate, ∿10%, containing about eight-fold concentrations of the wastewater constituents, were evaluated for chemical recovery. The concentrate, of course, contained the many chemicals associated with scouring, desizing, dyeing, and finishing. The straight-forward recycle of the concentrate from total plant composite wastewater without especially developed procedures was not expected. The chemical analyses of the concentrates obtained are tabulated in Tables 12 - 14.

Brief summaries of the tests conducted by each mill to evaluate concentrate reuse are included here as well as in more detail in the appendices.

Plant #50

The samples taken for reuse evaluation were misplaced in transit from the site to the corporate central dye laboratory; no reuse evaluations were conducted.

Plant #60

The attempts by the laboratory to use the concentrate in standard production procedures had limited success. The composite waste concentrate

TABLE 12. CHEMICAL ANALYSES OF SPIRAL-WOUND CELLULOSE ACETATE MEMBRANE CONCENTRATE WATER EVALUATED FOR REUSE

PLANT	#50	#60	#70	#40
% RECOVERY	90%	92%	90%	90%
PARAMETER[a]				
COD	5233	7650	3300	5020
BOD	285	1800	260	1800
TOC	1570	1800	750	1200
Alkalinity	390	160	-70	270
Hardness	10	50	70	105
Total Solids	3250	6314	3620	12210
Dissolved Solids	3182	6303	3608	12120
Volatile Solids	1764	3504	1680	2698
Color	2000	1500	450	2500
Turbidity	250	60	50	400
Conductivity	2500	2700	2500	13600
Phenol	0.65	-	0.08	0.21
pH	7.1	5.8	4.9	6.4
Mercury	<0.01	<0.01	0.003	<0.001
Manganese	0.12	1.32	0.56	0.25
Calcium	1.48	3.77	2.25	0.74
Iron	2.09	8.48	1.37	3.80
Nickel	<0.01	<0.01	0.21	0.10
Chromium	0.11	-	0.21	3.60
Zinc	0.88	-	9.22	9.30
Copper	0.12	0.50	0.73	5.50
Magnesium	0.70	1.30	1.19	2.17

TABLE 12. (continued)

PLANT	#80	#82	#83
% RECOVERY	90%	90%	90%
PARAMETER[a]			
COD	468	3620	2700
BOD	120	760	210
TOC	78	729	2000
Alkalinity	-85	170	220
Hardness	170	140	220
Total Solids	4650	10710	7030
Dissolved Solids	4645	10683	6987
Volatile Solids	370	1440	1770
Color	65	450	1400
Turbidity	20	70	770
Conductivity	5500	14500	6800
Phenol	0.03	0.09	0.08
pH	3.6	6.6	7.0
Mercury	<0.001	<0.001	<0.001
Manganese	<0.01	0.39	<0.01
Calcium	0.72	2.74	1.62
Iron	7.75	11.74	0.98
Nickel	0.76	1.41	<0.01
Chromium	0.58	0.33	0.07
Zinc	9.91	18.32	0.39
Copper	1.78	2.01	<0.01
Magnesium	1.62	12.23	10.5

[a] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE 13. CHEMICAL ANALYSES OF SELAS DYNAMIC MEMBRANE MODULE CONCENTRATE EVALUATED FOR REUSE

PLANT	#50	#60	#70	#40
% RECOVERY	90%	92%	90%	90%
PARAMETER[a]				
COD	4880	4560	4850	5020
BOD	170	66	840	1800
TOC	1371	1457	480	1200
Alkalinity	95	70	400	270
Hardness	30	14	45	105
Total Solids	2352	3148	5790	12210
Dissolved Solids	2276	3109	5786	12120
Volatile Solids	1328	2138	2050	2698
Color	2800	1800	960	2500
Turbidity	300	100	50	400
Conductivity	1250	1000	4500	13600
Phenol	7.9	0.02	0.22	0.21
pH	6.7	6.4	7.4	6.4
Mercury	<0.01	<0.01	<0.001	<0.001
Manganese	0.09	0.30	0.49	0.25
Calcium	3.55	1.42	3.16	0.74
Iron	2.66	0.94	1.06	3.80
Nickel	<0.01	0.06	0.49	0.10
Chromium	0.20	-	<0.01	3.60
Zinc	1.44	-	0.56	9.30
Copper	0.20	0.11	0.21	5.51
Magnesium	1.78	1.03	1.09	2.17

TABLE 13. (continued)

PLANT	#80	#81	#82	#83
% RECOVERY	90%	90%	90%	90%
PARAMETER[a]				
COD	1128	17800	3620	2700
BOD	300	6200	760	210
TOC	282	-	729	2000
Alkalinity	320	1300	170	220
Hardness	70	210	140	220
Total Solids	4880	18010	10710	7030
Dissolved Solids	4807	17810	10683	6987
Volatile Solids	1380	10870	1440	1770
Color	750	4000	450	1400
Turbidity	580	900	70	770
Conductivity	4600	6800	14500	6800
Phenol	0.27	1.40	0.09	0.08
pH	8.0	7.1	6.6	7.0
Mercury	<0.001	<0.001	<0.001	<0.001
Manganese	0.07	3.97	0.39	<0.01
Calcium	0.01	6.31	2.74	1.62
Iron	3.80	9.02	11.74	0.98
Nickel	0.58	2.12	1.41	<0.01
Chromium	0.44	1.38	0.33	0.07
Zinc	1.77	7.76	18.3	0.39
Copper	0.58	1.59	2.01	<0.01
Magnesium	1.43	11.36	12.23	10.5

[a] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE 14. CHEMICAL ANALYSES OF WESTINGHOUSE TUBULAR CELLULOSE ACETATE MEMBRANE MODULE CONCENTRATE EVALUATED FOR REUSE

PLANT	#50	#60
% RECOVERY	90%	92%
PARAMETER[a]		
COD	5233	7650
BOD	285	1800
TOC	1570	1800
Alkalinity	390	160
Hardness	10	50
Total Solids	3250	6314
Dissolved Solids	3182	6303
Volatile Solids	1764	3504
Color	2000	1500
Turbidity	250	60
Conductivity	2500	2700
Phenol	0.65	-
pH	7.1	5.8
Mercury	<0.01	<0.01
Manganese	0.12	1.32
Calcium	1.48	3.77
Iron	2.09	8.48
Nickel	<0.01	<0.01
Chromium	0.11	-
Zinc	0.88	-
Copper	0.12	0.50
Magnesium	0.70	1.30

[a] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

contained a complex mixture of dyes which dyed the carpet fabric a dull or dark shade.

Plant #70

The attempts by the laboratory to use the concentrate in standard production procedures were not successful. The composite waste contained only small quantities of dye. No attempts were made to determine special formulations and corresponding dye savings.

Plant #40

The concentrate from the composite wastewater was very strong, containing 12,210 mg/ℓ total solids, and 5020 mg/ℓ of COD. The total solids are mostly salts as indicated by the high (78%) percentage of non-volatile substances in the concentrate.

The concentrates resulting from both 70% and 95% recoveries were evaluated in the laboratory for a pad-dry-thermosol-steam procedure. Minimal dye concentration was obtained on the treated fabric giving evidence of small concentrations of a mixture of dyes and chemicals in the concentrate. No value could be observed from reuse of the concentrate obtained from the composite waste stream.

A sample of indigo rinse water was concentrated by the hyperfiltration membranes to evaluate the recovery of indigo dye. The concentrate obtained was then evaluated by plant laboratory personnel. The results indicated that the concentrated indigo rinse water could be used to formulate a dyeing solution suitable for reuse with equivalent fastness properties to the original dye. A significant savings of indigo was indicated by the laboratory results.

Plant #80

There was the possibility of recovering chemicals from isolated process streams and because of this rinse water from the desizing, mercerizing, and continuous dye ranges were subjected to hyperfiltration concentration.

The concentrates were evaluated by running white fabric through the concentrate in the dye pad, but omitting dyestuff. All dyeing chemicals were included. Samples were taken after the thermosol to check yellowing at this point.

Recycling of dyestuff in the concentrate was not possible as we received them in this evaluation. It is not known if special handling of the concentrate and/or further processing would bring this into the realm of possibilities. The precipitation or agglomeration of the dyestuff in the concentrate caused "dye spots" on several of the fabrics when run on the Benz range using dyeing chemicals only. Yellowing of the fabric after thermosol fixing would also have to be considered.

Plant #81

The concentrate resulting from 75% and 90% recoveries were evaluated in the laboratory for a pad-dry-thermosol-steam procedure. The concentrate from the total waste composite was not suitable for all dyebaths as dinginess and slight discoloration were noted on the dye blank in the dyeing sequences: sulfur, brine (reactive), and caustic/hydrosulfite. No value could be observed from reuse of the concentrate obtained from the composite waste stream.

There is the possibility of recovering dye from isolated process waste streams. Because of this possibility, steamer water overflow from the continuous dye range was subjected to hyperfiltration concentration.

Steamer water overflows from the processing of sulfur/disperse, disperse, vat/disperse, and fiber reactive/disperse dye systems were treated to 95 - 97.5% recovery (concentrating the dyes by factors of ∿15 to 30). Test dyeings made with these concentrates resulted in much lighter color values than the original dye system and light fastness was not satisfactory. Disperse dyes were apparently fixed during the thermosol process and therefore were not available in the steamer rinse. Vat dyes were concentrated satisfactorily, however.

Plant #82

The concentrates resulting from 75% and 90% recoveries were evaluated in the laboratory for a package dye system. The staining caused by the chemicals and dyes present in the concentrate made the final yarn unsuitable for commercial use. Without process modification it was adjudged impossible to recover the dyes or chemicals in the concentrate.

Plant #83

The attempts by the laboratory to use the concentrate in standard production procedures were not successful. The composite waste contained only small quantities of dye. No attempts were made to determine special formulations and corresponding dye savings.

REUSE SUMMARY

In all the plants studied it was observed that it is possible to eliminate some of the auxiliary chemicals. For example, with direct dyeing of cellulose, salt can be eliminated by using higher concentrations of dye in the dyebath. Excess dyestuffs will be recovered by the membranes for reuse in the next cycle. Depending on the amount of fiber dyed and range of colors, this modification may or may not be practical. Water, chemical, and energy prices will play a major role in the selection of dyeing processes, including recovery/reuse techniques, used in the future.

TREATABILITY

Most of the dyes, salts, and other chemicals are concentrated by membranes into the 10% of the wastewater not recovered as purified product water. Reuse of this concentrate may be technically feasible in some instances with process modification. However, disposal of the concentrate is of significant concern.

The treatability of the concentrate was examined in a bench-scale biological reactor. The treatment efficiency of chemical coagulation and of carbon adsorption were also evaluated. The results of these tests are summarized in Table 15. The characteristics of the concentrated wastewater for six plants are presented in Table 16. A discussion of the results for each mill is included in the appendices.

From the treatability results in Table 15 for six plants, it is concluded that hyperfiltration of the composite waste streams produces a concentrate that is as treatable as the raw plant effluents. Therefore, the existing biological treatment system operating at the plants studied could be utilized with hyperfiltration concentrate. Because the volume flow of concentrate would be about one-tenth of the present flow, horsepower requirements for aeration would be decreased, and suspended solids removal would be improved significantly.

TABLE 15. A SUMMARY OF OVERALL BEST RESULTS FOR TREATMENT METHODS

Plant	Percent Removal					
	#60	#70	#40	#80	#81	#82
Biological Study[a]						
BOD_5	86	89	39[e]	95	98	97
COD	44	60	29	83	65	64
Color[b]	16	0	0	27	75	0
Biological Study with Carbon Added						
BOD_5	97	92	36	99	99	95
COD	72	63	35	88	66	63
Color[b]	56	0	0	51	76	0
Alum Treatment[c]						
BOD_5	9	27	14	60	15	38
COD	10	23	23	78	14	45
Color[b]	0	9	0	76	48	65
Powdered Activated Carbon[d]						
BOD_5	61	29	76	72	35	23
COD	73	19	69	60	32	52
Color[b]	62	67	67	71	80	53

[a] Percent removal based on the results for the entire period including time before and after 1000 mg/ℓ carbon addition. Removal based on decantate sample compared to the raw reactor feed.

[b] Unfiltered or "apparent" color.

[c] Data for the alum treatment based on the best treatment, 500 mg/ℓ in all cases. Removal based on decanted sample after floc settling compared with the feed.

[d] Data for the carbon treatment based on the best overall treatment, 5000 mg/ℓ in all cases. Removal based on a treated filtered sample compared with the untreated filtered raw feed.

[e] Probably the result of grab sample for this test since waste treatment plant functions normally.

TABLE 16. CONCENTRATE WASTE CHARACTERIZATION

Non-metal Analyses[a]	#60	#70	#40	#80	#81	#82
COD	2500	3720	15285	4032	8871	2496
Filtered COD					7942	2487
TOC	935	1410	5753	707	4140	1606
BOD	270	1078	1547	561	3745	860
BOD	415	1600	2200	300	4800	925
BOD	515	1800	3500	475	4450	1175
BOD	560	1600	4500	700	4700	1100
BOD	820	2200	5000	425	3000	450
Solids						
Total	3760	5028	10028	9870	8702	4334
Dissolved	3000	4803	9853	9785	8347	4106
Suspended	760	225	175	85	355	228
Volatile	2030	2104	4050	1254	5074	1714
pH	6.7	6.0	6.6	6.8	7.0	5.0
Color (Pt-Co units)	1250	1000	12044	2618	5618	1826
Turbidity (FTU)	43	3	opaque	0.38	opaque	15
Conductivity	2000	3900	9000	9600	5000	4000
Alkalinity	140	456	587	182	341	65
Hardness	32	57	74	135	75	97
Ammonia Nitrogen	24	5	3	3	4	12
Total Kjeldahl Nitrogen	25	11	6	6	10	14
Phosphorus	160	4.2	15	6	41	3.0
Phenols	1.0	0.40	0.52	0.1	0.1	0.1

TABLE 16. (continued)

Metal Analyses[a]	#60	#70	#40	#80	#81	#82
Calcium	2.4	4.0	2.1	5.9	3.7	8.5
Chromium	0.13	0.19	8.1	3.1	1.4	-
Copper	0.2	1.2	8.6	0.64	0.66	6.2
Iron	1.3	1.3	10.3	12.0	7.0	2.9
Magnesium	1.0	6.0	12.0	13.0	24.0	-
Manganese	0.53	0.08	0.28	0.43	1.8	0.27
Mercury (μg/ℓ)	-	6.0	-	5.5	6.0	1.0
Nickel	0.33	0.17	1.2	1.9	0.1	0.56
Zinc	2.9	3.4	5.2	5.0	3.0	20.0

[a] Unless otherwise indicated, all units are in mg/ℓ with the exception of pH, which is unitless.

SECTION 7

MEMBRANE PERFORMANCE

Following the accumulation of water samples for reuse evaluation, the performance tests of membranes were conducted. The duration of each test was about 200 hours to allow equilibration of operating conditions and membrane performance. The duration of each test is tabulated in Table 17.

The performance of membranes is characterized by the flux and the rejection. In all tests with wastewater, the flux initially declined sharply but equilibrated to a nearly constant value. The rejection, however, was usually constant or increased. The productivity of the membrane units were designed using the equilibrium value of flux.

An important parameter effecting the membrane performance is the temperature of the wastewater. The influence of temperature was evaluated for the high-temperature membranes after the stable flux was reached at each plant. The strong increase of flux was observed in each case.

FLUX DECLINE AND REJECTION

For all membranes evaluated in this study a significant decline in flux was observed during the initial portion of the 200-hour performance tests. In Figures 3 and 4 examples of the observed flux declines are presented. In Figure 3 for the dynamic Zr-PAA membranes on three modules (#4, #10, and #19) of ceramic tubes, the flux decline is quite severe. The flux does quickly achieve what is apparently a stable equilibrium value. (The equilibrium value is used in the cost projections in Section 8.)

It may be important to note that the two to one range in fluid velocities does not appear to effect the flux decline. Also, the rejection increases significantly indicating an improvement in the quality of the permeate. This increased rejection suggests some self-forming membrane layer. The lack of a significant velocity effect and the increasing rejection indicates that the flux decline is not simply a classical fouling by particulates. Similar results are shown in Figure 4 for a spiral-wound cellulose acetate membrane.

Two points can be made from the observations about flux decline. First, design flux based on the equilibrium values yields much higher cost estimates than would result from the initial flux characteristics of new membranes evaluated in laboratory systems with just salt water. The potential improvement in economics of membranes if flux decline could be presented in very large. Second, the flux decline may be of a different nature than the

TABLE 17. TABULATION OF MEMBRANE EVALUATION TESTS AND TEST DURATION[a]

Plant	Selas Dynamic	UOP Spiral-wound Cellulose Acetate	Westinghouse Tubular Cellulose Acetate	Westinghouse Tubular Polysulfone
	Test Duration, hours			
#50	270[b]	250	250	
#60	450[c]	450	450	
#70	200	200		
#40	200			200
#80	200			
#81	200			
#82	200	200		200
#83	200	87		

[a] Membranes evaluated depended on availability.

[b] Two test sequences of 200 and 70 hours were conducted.

[c] Two test sequences of 110 and 340 hours were conducted.

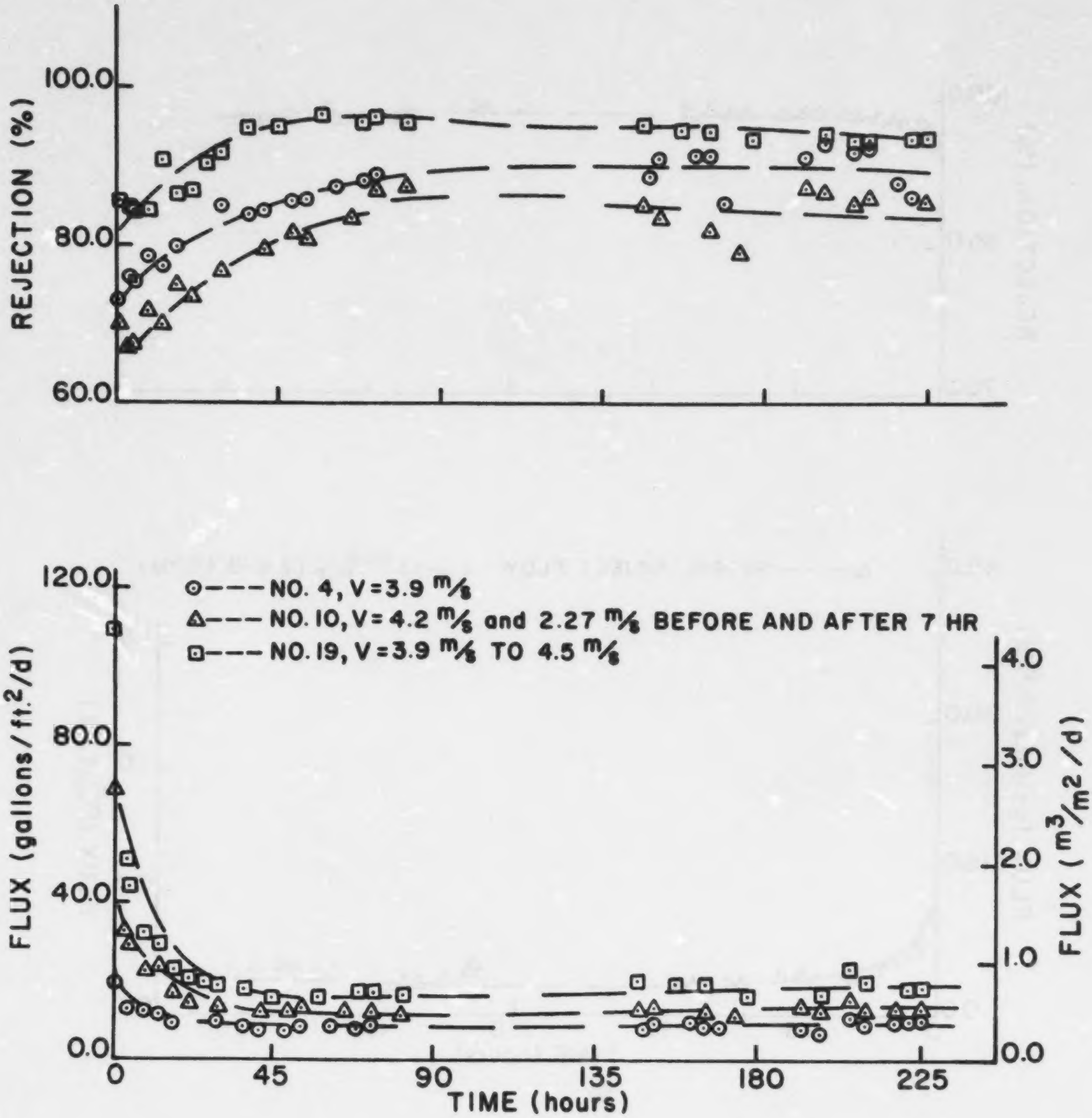


Figure 3. Flux decline and conductivity rejection of dynamic membrane Modules #4, #10, and #19 with untreated textile wastewater with feed velocities (V) as indicated.

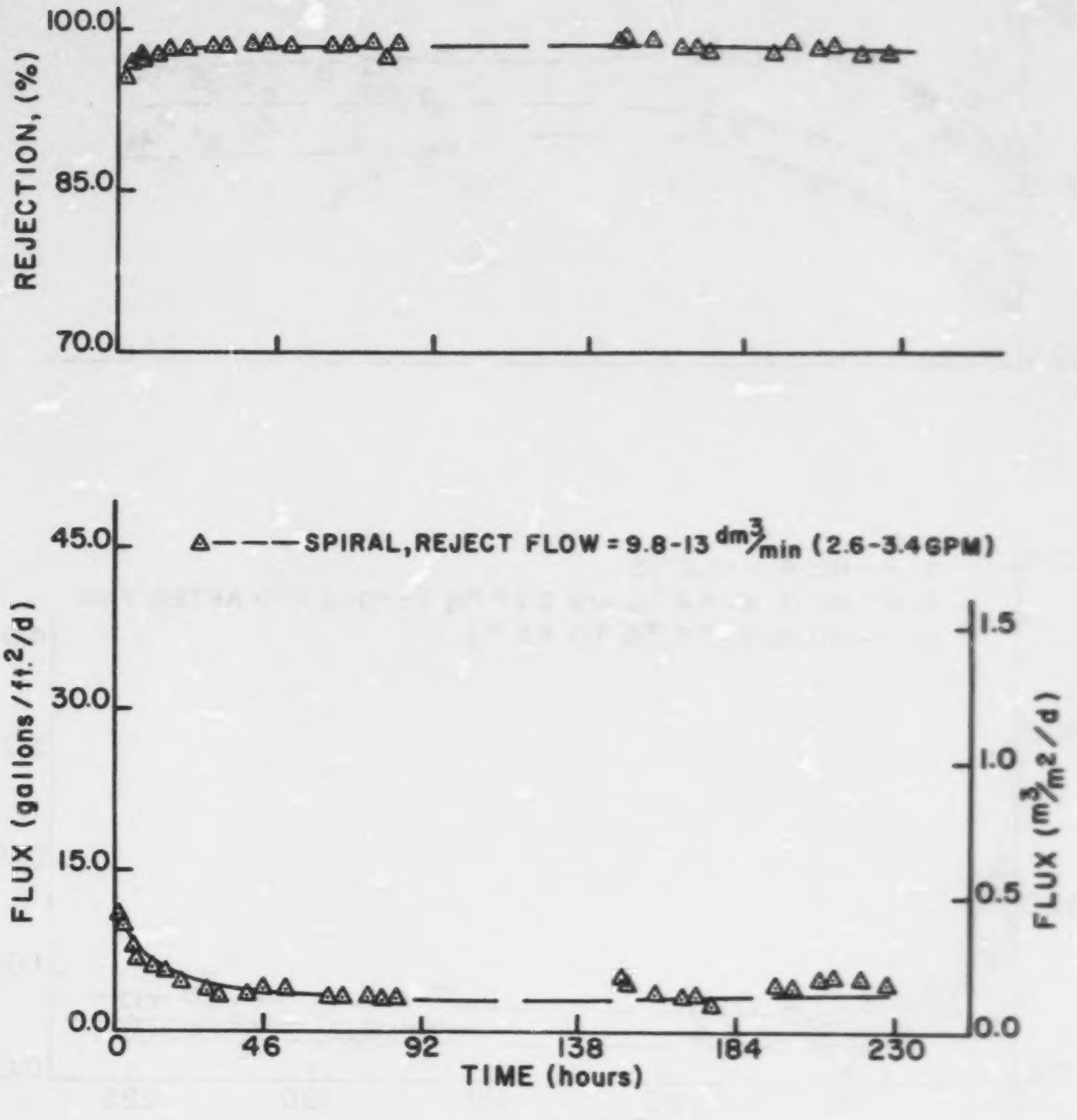


Figure 4. Flux decline and conductivity rejection of spiral-wound cellulose acetate membranes with untreated textile wastewater.

classical particulate fouling studied for deslating of natural waters. In almost every case the quality of the permeate, as evidenced by increased membrane rejections, increased as the flux declined.

TEMPERATURE EFFECT

Because of the significance of membrane flux on capital and operating costs, the strong influence of temperature was studied at each plant. All the data are empirically correlated by

$$\ln \left(\frac{J}{J_1}\right) = k \left[\frac{1}{T_1} - \frac{1}{T}\right]$$

where J_1 is the flux at reference temperature T_1 in degrees K. The constant, k, is determined empirically for each plant. Twenty-five temperature scans were performed using Zr(IV)-PAA membranes during the course of on-site evaluation of membrane performance at the eight mills. Values of k determined from the excursions varied widely depending on the feed being processed and past exposure of the membranes. The mean value is k = 3280°K with variation from 5310°K to 1860°K. For example, the flux at 90°C is from four to ten times the flux at 25°C. The data indicate that qualitatively the temperature effect is not altered by flux decline.

Two benefits can be realized from processing high-temperature wastes with membranes: (1) the exponential rise in flux with temperature results in a reduced capital expenditure for membrane units capable of handling the flow, and (2) energy savings can be realized by returning hot reusable water to the process and heating only the made-up fraction. The net advantage of the above benefits may be reduced by the tendency of high flux membranes to foul more quickly, i.e., higher circulation velocity (and therefore more pumping power) may be required to prevent flux declines at higher fluxes.

SECTION 8

COST ESTIMATES

The equipment performance data are used in the following cost projections for full-scale treatment plants. The cost projections include pretreatment, i.e., pH control, temperature control, and suspended solids removal, as required for the two membrane types. However, no allowance is included for storage reservoirs, nor for the 10 - 20% makeup water (10 - 15% due to evaporation and drying), nor for treatment of the concentrate. Cost projections presented are incremental costs that may be useful in a more detailed economic analyses. Because cost for taxes, insurance, and overhead may vary widely from plant to plant and from time to time, no estimates for these costs are included.

The cost projections presented in Tables 18 and 19 are based on the more detailed cost study for La France.[6] This current study assumed that: (1) pretreatment (operating and capital) cost, auxiliary equipment, engineering, and electrical costs are proportional to the volume of water processed, (2) the membrane housing, maintenance, and membrane replacement costs are inversely proportional to the flux and proportional to volume of water processed, and (3) labor costs are assumed at three man-years/year for each system. These cost-scale factors are the result of the modular character of membrane equipment. Of course, some economy of size may be realized in terms of labor costs and instruments and controls.

Amortization costs, included in total operating costs, were determined by converting capital costs to equivalent annual costs assuming 10% interest for ten years with no salvage value. The lifetime for cellulose acetate membranes was assumed to be three years. Lifetime of dynamic membrane supports was assumed to be ten years, with membrane replacement performed in-situ annually.

Table 18 summarizes the costs of cellulose acetate membranes for processing composite waste. The flux data obtained in the La France project[6] are the basis for determining the required membrane area. The total cost ranges from ∿\$1.17/kgal to ∿\$1.47/kgal (∿31¢/m^3 to ∿39¢/m^3). The major cost item is the membrane replacement cost. Membrane replacement cost was based

TABLE 18. COSTS OF CELLULOSE ACETATE MEMBRANES PROCESSING COMPOSITE WASTE AT EIGHT MILLS

PLANT	#50	#60	#70	#40
INSTALLED CAPACITY, m^3/d	9,470	3,788	1,892	20,833
CAPITAL COSTS, \$ x 10^{-3}				
Pretreatment:				
Prefilter	\$ 44	\$ 18	\$ 9	\$ 96
Cooling	300	a	60	660
pH Control	b	b	b	22
Membrane Housings	267	110	52	588
Auxiliary Equipment	148	59	29	324
Engineering	375	150	75	825
Contingency (10%)	113	34	23	252
TOTAL	\$1,247	\$371	\$248	\$2,767
OPERATING COST, \$/d				
Pretreatment	56.25	22.50	11.30	123.80
Labor (3 man-years/year)	126.28	126.28	126.28	126.28
Maintenance	68.60	28.43	13.48	151.00
Electric Power (2¢/kWh)	357.00	142.80	71.40	785.00
Membrane Replacement[c]	1,776.65	735.80	349.50	3,919.67
Amortized Capital[d]	811.80	241.52	161.45	1,801.32
TOTAL	\$3,196.58	\$1,297.33	733.41	\$6,907.07
TOTAL COST[e], ¢/1000 gal	127.90	129.70	146.80	125.60
¢/m^3	33.80	34.20	38.80	33.20

TABLE 18. (continued)

PLANT	#80	#81	#82	#83
INSTALLED CAPACITY, m^3/d	11,364	30,303	7,576	24,409
CAPITAL COSTS, $\$ \times 10^{-3}$				
Pretreatment:				
Prefilter	$ 53	$ 140	$ 35	$ 131
Cooling	360	960	a	a
pH Control	12	32	b	30
Membrane Housings	321	855	218	802
Auxiliary Equipment	117	472	118	442
Engineering	450	652	140	521
Contingency (10%)	131	311	51	193
TOTAL	$1,444	$3,422	$562	$2,119
OPERATING COST, $/d				
Pretreatment	67.50	180.00	45.00	168.80
Labor (3 man-years/year)	126.28	126.28	126.28	126.28
Maintenance	82.66	219.86	56.16	206.00
Electric Power (2¢/kWh)	428.40	1,142.40	285.60	1,071.00
Membrane Replacement[c]	2,141.48	5,696.32	1,454.74	5,343.75
Amortized Capital[d]	940.04	2,227.72	365.86	1,379.47
TOTAL	$3,786.36	$11,571.58	$2,333.64	$8,295.30
TOTAL COST[e], ¢/1000 gal	126.20	144.60	116.70	128.70
¢/m^3	33.30	38.20	30.80	34.00

[a] Cellulose acetate membranes can operate at up to 38°C (100°F).
[b] Cellulose acetate membranes have a pH range of 4 - 8.
[c] Assuming: 3 yr membrane life, 10% interest over 10 yrs, no salvage value, 250 d/yr.
[d] Assuming: 10 yr life, 10% interest, no salvage value, 250 d/yr.
[e] Does not include costs for taxes, insurance, or overhead.

upon an assumed membrane life of three years, as recommended by the manufacturer. Longer or shorter life will have a major influence on the operating cost. Pretreatment costs[a] are based on the La France study.

Table 19 summarizes the costs of dynamic membranes for processing composite wastewater. The flux data obtained in the 200-hour tests at each mill are used to determine the required membrane area. The costs range from ∿\$2.36/kgal to ∿\$5.59/kgal (∿64¢/m^3 to ∿\$1.47/m^3). The major cost item is the amortization of capital. However, the reoccurring cost for membrane replacement is insignificant.

A combined membrane system design is possible where the more expensive dynamic Zr(IV)-PAA membranes with high-temperature capability are used on the hotter (∿25%) of the effluent flow and the less expensive cellulose acetate membranes are used on the cooler (∿75%) of the effluent flow. In such a combined system no cooling of the wastewater is necessary before being processed by the cellulose acetate membranes. In addition, the dynamic membranes will produce a small volume of hot water for recycle and may lead to significant energy conservation. Any possible advantages of a combined membrane system are dependent on the temperature of the effluent being processed, and the needs for recycled hot water.

No attempt was made to optimize the condition of the wastewater by pretreatment. It was recognized, however, that there is a potential to reduce hyperfiltration costs significantly by maintaining the initially-high membrane flux. The restoration of flux by washing must be taken into account with the subsequent flux decline to establish a frequency of cleaning and a corresponding time-average flux. The operation of membranes at the highest temperature is a strong influence on achieving high membrane flux. Of course, treatment of "hot" wastewater also maximized the value of thermal energy recycle.

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[a] Information presented by Dr. K. C. Channabasappa at the Membrane Separation Technology Seminar at Clemson University in August, 1977, indicates pretreatment costs approximately equal membrane costs for spiral-wound and hollow-fiber systems used in desalination of natural water. Pretreatment may be expected to be even higher for industrial wastewater.

TABLE 19. COSTS OF DYNAMIC MEMBRANES PROCESSING COMPOSITE WASTE AT EIGHT MILLS

PLANT	#50	#60	#70	#40
INSTALLED CAPACITY, m^3/d	9,470	3,788	1,892	20,833
CAPITAL COSTS, $\$ \times 10^{-3}$				
Pretreatment:				
Prefilter	$ 31	$ 13	$ 6	$ 69
Cooling	a	a	a	a
pH Control	b	b	b	22
Membrane Housing and Supports	9,390	5,129	1,025	15,822
Auxiliary Equipment	148	59	29	324
Engineering	375	150	75	825
Contingency (10%)	994	535	114	1,706
TOTAL	$10,937	$5,886	$1,249	$18,768
OPERATING COST, $/d				
Pretreatment	6.25	2.50	1.30	13.80
Labor (3 man-years/year)	126.28	126.28	126.28	126.28
Maintenance	710.86	338.30	34.52	1,198.00
Electric Power (2¢/kWh)	1,560.00	624.00	312.00	3,432.00
Membrane Replacement[c]	56.84	31.05	6.21	95.80
Amortized Capital[d]	7,119.99	3,831.79	813.10	12,217.97
TOTAL	$9,580.22	$4,953.92	$1,293.41	$17,083.85
TOTAL COST[e], ¢/1000 gal	383.20	495.40	259.09	310.60
¢/m^3	101.20	130.80	68.40	82.00

TABLE 19. (continued)

PLANT	#80	#81	#82	#83
INSTALLED CAPACITY, m^3/d	11,364	30,303	7,576	28,409
CAPITAL COSTS, $ x 10^{-3}				
Pretreatment:				
Prefilter	$ 38	$ 100	$ 25	$ 94
Cooling	a	a	a	a
pH Control	b	32	b	b
Membrane Housing and Supports	5,753	16,419	5,753	44,950
Auxiliary Equipment	117	472	118	442
Engineering	450	1,200	300	1,125
Contingency (10%)	642	1,822	620	4,664
TOTAL	$7,059	$20,045	$6,816	$51,305
OPERATING COST, $/d				
Pretreatment	7.50	20.00	5.00	18.80
Labor (3 man-years/year)	126.28	126.28	126.28	126.28
Maintenance	435.55	1,242.97	435.55	3,403.00
Electric Power (2¢/kWh)	1,872.00	4,832.00	1,248.00	4,680.00
Membrane Replacement[c]	34.83	99.40	34.83	272.00
Amortized Capital[d]	4,595.41	13,049.30	4,437.22	33,399.56
TOTAL	$7,071.57	$19,369.95	$4,286.88	$41,899.64
TOTAL COST[e], ¢/1000 gal	235.70	242.10	314.30	558.70
¢/m^3	62.20	63.90	83.00	147.50

[a] Dynamic membranes require no temperature control.
[b] Dynamic membranes have a pH range of 4 - 10.
[c] Assuming: 1 yr membrane life, 250 d/yr.
[d] Assuming: 10 yr life, 10% interest, no salvage value, 250 d/yr.
[e] Does not include costs for taxes, insurance, or overhead.

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APPENDIX A

SCREENING TESTS

Each of the twelve plants involved in the study sent 0.4 m^3 (100-gallon) samples of total plant effluent to Clemson University for laboratory-scale tests. These screening tests were conducted to provide preliminary indications of (1) membrane performance, and (2) reusability of the renovated water and residual concentrate. These preliminary results provided part of the basis for the selection of the mills to be included in the on-site test program.

MEMBRANE PERFORMANCE

A series of hyperfiltration tests were performed at Clemson to provide preliminary data to evaluate membrane performance when applied to total plant effluent from each of the twelve participating plants. These data were considered when selecting the plants to participate in the on-site testing phase of the program.

Each of the twelve participating mills shipped a 0.4 m^3 (100-gallon) sample of their plant outfall to Clemson. Plant #81, Plant #40, and Plant #80, in addition to the combined effluent, sent 0.4 m^3 samples of selected waste from inside the mill to be evaluated.

Membranes tested were the dynamically formed Zr(IV)-PAA on Selas ceramic tube supports, the Westinghouse (now Union Carbide) tubular cellulose acetate, and the UOP spiral-wound cellulose acetate.

Tables A-1 through A-4 show a summary of the screening tests by membrane type. Reference parameters indicate membrane performance with a 1000 mg/ℓ NaCl solution prior to each screening test. Wastewater performance parameters are the final values at the end of each test. Table A-4 shows results of tests performed utilizing a Selas Zr(IV)-PAA membrane exposed to over 3000 hours of operating time prior to these screening tests.

Results of screening tests on composite effluents show 85 - 90% conductivity rejections, indicative of high quality reusable product water and near total removal of color in every case. Due to the limited time exposure membrane flux results were considered inconclusive. There were no catastrophic experiences with the flux decline even though pretreatment was limited to just pH adjustment (where required for cellulose acetate membranes) and 25-micron filtration.

TABLE A-1. PERFORMANCE OF NEW DYNAMIC HYPERFILTRATION MEMBRANES DURING SCREENING TESTS

	Reference[a]			Performance with Wastewater[b]				
Plant	Flux (m^3/m^2-d)	Rejection (%)	Temp. (°C)	Flux (m^3/m^2-d)	Temp. (°C)	Conductivity Rejection(%)	Color (%) Rejection	pH[c]
#83	3.1	87.0	30	1.4	50	93	99	8.5
#43	-	-	-	1.3	50	93	99	8.7
#81 (PVA)	-	-	-	0.1	81	48	-	6.9*
#81 (PVA)	-	-	-	0.1	81	67	-	6.9*
#81 (PVA)	-	-	-	0.1	81	67	-	6.9*
#81	-	-	-	13.3	64	72	99	11.0*
#81	-	-	-	10.2	65	51	99	11.0*
#80[d] (2)	-	-	-	5.1	66	62	99	11.0*
#40[d] (1)	2.3	92.5	38	3.1	60	97	99	6.6
#80[d] (3)	7.9	95.2	47	3.5	62	93	99	8.2*

TABLE A-1. (continued)

	Reference[a]			Performance with Wastewater[b]				
Plant	Flux (m^3/m^2-d)	Rejection (%)	Temp. (°C)	Flux (m^3/m^2-d)	Temp. (°C)	Conductivity Rejection(%)	Color (%) Rejection	pH[c]
#40[e] (2)	3.8	91.0	35	3.9	55	96	99	8.8
#42	3.5	95.4	32	3.7	60	93	99	8.6
#82	-	94.0	-	4.2	65	91	99	8.5
#50	3.7	92.0	33	4.5	61	82	99	6.4*
#60	3.7	90.0	50	4.2	61	94	99	6.7
#70	4.1	90.0	55	3.8	61	93	95	7.0
#44	3.7	90.0	53	3.5	61	91	99	7.8*
#80[d] (5)	4.1	91.0	53	4.5	55	94	99	6.8
#41	4.5	90.0	55	3.0	64	93	99	8.2
#81 (PVA)[f]	-	-	-	1.3	65	27	99	6.7*

[a] Sodium chloride solution, 1000 mg/ℓ.

[b] Operating conditions: Pressure = 6.55 MPa (950 psig); recovery = 77%; membrane age = up to 300 hours.

[c] pH of raw feed adjusted prior to test except as indicated by asterisk.

[d] Plant #80 effluents: 1 = finishing basement, 2 - preparation basement, 3 - dyehouse, 4 - mercerizing, 5 - composite.

[e] Plant #40 effluents: 1 - preparation, 2 - composite.

[f] Ultrafiltration membrane used.

TABLE A-2. PERFORMANCE OF UOP CELLULOSE ACETATE MEMBRANES DURING SCREENING TESTS

	Reference[a]		Performance of Wastewater[b]			
Plant	Flux (m^3/m^2-d)	Rejection (%)	Flux (m^3/m^2-d)	Conductivity Rejection(%)	Color (%) Rejection	pH[c]
#83	0.68	96	0.48	98	99	6.8
#43	0.71	95	0.49	98	-	8.5
#82	0.56	96	0.59	95	99	6.6-7.8*
#50	0.67	94	0.45	95	99	5.3
#81	0.74	94	0.15	99	99	6.0
#44	0.51	96	0.35	97	99	6.4
#80[d] (5)	0.61	96	0.54	98	99	6.8
#42	0.59	96	0.50	97	99	7.0*
#80[d] (4)	0.56	95	0.51	97	99	6.8
#70	0.42	97	0.33	89	99	4.0*
#40	0.38	97	0.17	92	99	4.4
#80[d] (3)	0.33	97	0.37	95	99	7.6
#80[d] (2)	0.44	94	0.40	-	-	11.0
#80[d] (1)	0.51	89	0.51	90	99	7.6
#60	0.53	84	0.44	94	96	6.4*
#41	0.43	85	0.16	89	99	5.2

[a] Sodium chloride solution, 1000 mg/ℓ.

[b] Operating conditions: Pressure = 2.76 MPa (400 psig); T = 32°C; inlet flow = 17 ℓ/min; recovery = 77%.

[c] pH of raw feed adjusted prior to test except as indicated by asterisk.

[d] Plant #80 effluents: 1 - finishing basement, 2 - preparation basement, 3 - dyehouse, 4 - mercerizing, 5 - composite.

TABLE A-3. PERFORMANCE OF WESTINGHOUSE CELLULOSE ACETATE MEMBRANES DURING SCREENING TESTS

	Reference[a]		Performance with Wastewater[b]			
Plant	Flux (m^3/m^2-d)	Rejection (%)	Flux (m^3/m^2-d)	Conductivity Rejection(%)	Color (%) Rejection	pH[c]
#80[d] (5)	0.84	91.2	0.77	97.8	91.8	6.8
#42	1.24	93.7	0.80	94.0	99.0+	7.0*
#80[d] (4)	0.94	92.2	0.87	92.4	98.2	6.8
#70	1.09	94.6	0.68	85.3	81.0	4.0*
#40[e] (2)	0.86	93.0	0.38	91.0	98.5	4.4
#80[d] (3)	0.86	93.0	0.37	92.2	93.1	7.6
#80[d] (2)	0.94	92.3	0.95	-	-	11.0
#80[d] (1)	1.22	89.0	1.14	90.8	99.0+	7.6
#60	1.27	81.0	1.00	91.2	98.0	6.4*
#41	1.01	87.0	0.44	88.7	97.0	5.2

[a] Sodium chloride solution, 1000 mg/ℓ.

[b] Operating conditions: Pressure = 2.76 MPa (400 psig); T = 32°C; inlet flow = 11.3 ℓ/min; recovery = 77%.

[c] pH of raw feed adjusted prior to test except as indicated by asterisk.

[d] Plant #80 effluents: 1 - finishing basement, 2 - preparation basement, 3 - dyehouse, 4 - mercerizing, 5 - composite.

[e] Plant #40 effluents: 1 - preparation, 2 - composite.

TABLE A-4. PERFORMANCE OF AGED[a] DYNAMIC HYPERFILTRATION MEMBRANES DURING SCREENING TESTS

	Reference[b]			Performance with Wastewater[c]				
Plant	Flux (m^3/m^2-d)	Rejection (%)	Temp. (°C)	Flux (m^3/m^2-d)	Temp. (°C)	Conductivity Rejection(%)	Color (%) Rejection	pH[d]
#81	-	-	-	4.0	65	83	99	11.0*
#80[e] (2)	2.5	85.4	32	4.0	66	76	99	11.0*
#40	2.5	86.0	38	4.0	60	91	99	6.6
#80[e] (3)	4.2	84.0	47	4.3	62	84	98	8.2
#50	-	-	-	4.7	61	88	99	6.4*
#60	4.0	77.5	50	4.0	61	89	99	6.7
#70	4.2	79.0	55	3.6	61	84	95	7.0
#44	3.7	79.0	53	3.3	61	82	99	7.8*
#80[e] (5)	3.4	78.0	53	2.6	61	87	99	6.8
#41	3.7	78.0	55	2.1	64	85	99	8.2

[a] Test module previously employed in hyperfiltration pilot plant (EPA Grant No. S800929) at La France.

[b] Sodium chloride solution, 1000 mg/ℓ.

[c] Operating conditions: Pressure = 6.55 MPa (950 psig); recovery = 77%; membrane age = 3000 hours.

[d] pH of raw feed adjusted except as designated by asterisk.

[e] Plant #80 effluents: 1 - finishing basement, 2 - preparation basement, 3 - dyehouse, 4 - mercerizing, 5 - composite.

WATER REUSE SCREENING TEST CONDUCTED AT DEERING MILLIKEN LABORATORY

The potential for reuse of the product water and concentrated residue was evaluated by laboratory dyeings conducted at Deering Milliken Research Laboratory. All but one of the mills involved in the project process both cotton and synthetic fibers. Samples of product water were evaluated with basic and disperse dye systems. The dye formula and procedures are given in Table A-5. The concentrates were evaluated by dyeing a fabric sample in a blank dye bath with no dyes present in the bath. This was done to determine the presence of recoverable dye. This dyeing procedure is given in Table A-6.

The results of these tests indicate that no problems will be encountered with the reuse of product water in textile plant dyeings.

The concentrate water samples contained significant quantities of dyestuff which stained the multifiber fabric and demonstrated the presence of disperse and direct dyes in many samples. The value of dye in any waste stream will depend on the plant production and the plant's ability to fit its reuse into normal production. This must be determined by more tests with each individual mill.

TABLE A-5. EVALUATION OF PRODUCT WATER WITH BASIC AND DISPERSE DYEING SYSTEMS

Basic Dye System

Migrasist AC	3.00%	on the weight of fabric
Sequesterant ST	0.25%	on the weight of fabric
Glaubers Salt	5.00%	on the weight of fabric
pH	4.00	
Basic Dyes		
Genacryl Yellow 4G	0.50%	on the weight of fabric
Genacryl Blue 3G	0.30%	on the weight of fabric
Astrazon Red 4G	0.50%	on the weight of fabric

Procedure

Add chemicals and dyes at room temperature. Add acrylic fabric and raise to 230°F with agitation. Dye at 230°F for 45 minutes. Cool bath to 200°F and rinse with water. Repeat with tap water for comparison.

Disperse Dye System

Acetic Acid to give pH = 4.0

Carolid JAL	4.00%	on the weight of fabric
Sequesterant ST	0.25%	on the weight of fabric
Disperse Dyes		
Palanil Yellow 3G	0.50%	on the weight of fabric
Palanil Pink REL	0.50%	on the weight of fabric
Resolin Blue FBL	0.50%	on the weight of fabric

Procedure

Add chemicals and dyes at room temperature. Add polyester fabric and raise to 266°F with agitation. Dye at 266°F for 30 minutes. Cool bath to 200°F and rinse with water. Repeat with tap water for comparison.

TABLE A-6. EVALUATION OF CONCENTRATE WATER WITH BLANK DYEBATHS FOR BASIC, DISPERSE, AND DIRECT DYEING SYSTEMS

Basic Dye System

Acetic Acid	2.00%	on the weight of fabric
Glaubers Salt	5.00%	on the weight of fabric
No dyes used		

Procedure

Add chemicals to concentrate water. Add multifiber fabric and raise to 230°F with agitation. Dye at 230°F for 60 minutes. Cool bath to 200°F and rinse with cold water.

Disperse Dye System

Acetic Acid	2.00%	on the weight of fabric
Dye Carrier	4.00%	on the weight of fabric
No dyes used		

Procedure

Add chemicals to concentrate water. Add multifiber fabric and raise to 266°F with agitation. Dye at 266°F for 60 minutes. Cool bath to 200°F and rinse with cold water.

Direct Dye System

Tetrasodiumpyrophosphate	1.00%	on the weight of fabric
Sodium Chloride	100%	on the weight of fabric
No dyes used		

Procedure

Add chemicals to concentrate water. Add multifiber fabric and raise to 180°F with agitation. Dye at 180°F for 30 minutes. Cool bath.

APPENDIX B

PLANT #50

The on-site tests conducted from December 10, 1974, to January 18, 1975, were to obtain the following information: (1) plant laboratory evaluation of reuse, and (2) engineering performance data with membranes. The samples taken for dye reuse evaluations were lost in transit to the corporate central laboratory, and hence no reuse dyeings were conducted. Plant #50 was not included in the concentrate treatability study because this part of the project was not authorized until after January, 1975.

FIBERS AND CHEMICALS

The dyeing and finishing processes at Plant #50 involve several different dyes and finishes. The dyeing is done in pressure jet and atmospheric beck dyeing machines. The principal dyes employed are disperse, acid, and direct dyes. The materials processed are polyester (65%), rayon (20%), and wool (15%).

Ninety percent of the 9091 m^3/d (2,400,000 gallons/day) total water usage is in the dyehouse. Allowing for evaporation in the dyehouse, the composite waste stream is at least 80% by volume dyehouse wastewater.

WASTEWATER CHARACTERISTICS

The variety of dyes and scouring chemicals used produce a complex and variable waste stream composition. The wastewater characteristics, based on a monthly average for the winter of 1975, of plant wastewater discharge parameters are: BOD_5 = 629 mg/ℓ; COD = 1919 mg/ℓ; total suspended solids = 70 mg/ℓ; total dissolved solids = 1511 mg/ℓ; pH = 4.5; temperature = 140°F. Tables B-1 and B-2 present the results of analyses for four grab samples obtained during the period of on-site testing. Plant #50 is classified as Subcategory 5, knit fabric finishing.[a]

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[a] Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Textile Point Source Category. EPA-440/1-74-022-a, US Environmental Protection Agency, Washington, DC, 1974.

TABLE B-1. CHEMICAL ANALYSES OF PLANT #50 WASTEWATER[a]

SAMPLE NUMBER	500	526
DATE TAKEN	1/6/75	1/10/75
PARAMETER[b]		
COD	608	2204
BOD	30	1150
TOC	103	-
Alkalinity	36	0
Hardness	34	-
Total Solids	490	790
Dissolved Solids	458	730
Volatile Solids	196	-
Color	400	-
Turbidity	70	168
Conductivity	360	360
Phenol	0.41	0.796
pH	6.6	4.2
Mercury	0.01	-
Manganese	0.15	-
Calcium	4.42	-
Iron	0.84	3.70
Nickel	0.06	0.15
Chromium	0.39	0.11
Zinc	0.45	3.680
Copper	0.1	0.74
Magnesium	3.28	-

[a] Grab samples of combined plant effluent.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE B-2. CHEMICAL ANALYSES OF PLANT #50 WASTEWATER[a]

SAMPLE NUMBER	532	538
DATE TAKEN	1/13/75	1/18/75
PARAMETER[b]		
COD	2584	2280
BOD	770	565
TOC	-	-
Alkalinity	0	0
Hardness	-	-
Total Solids	2768	2276
Dissolved Solids	2612	2244
Volatile Solids	-	-
Color	-	-
Turbidity	350	350
Conductivity	2300	2400
Phenol	0.093	0.093
pH	3.5	3.5
Mercury	-	-
Manganese	-	-
Calcium	-	-
Iron	0.48	0.53
Nickel	0.11	0.07
Chromium	0.11	0.11
Zinc	5.595	9.075
Copper	0.31	0.26
Magnesium	-	-

[a] Grab samples of combined plant effluent.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

SCHEDULE AND PROCEDURE

Schedule

The mobile hyperfiltration laboratory was started up at Plant #50, the first plant participating in the on-site testing portion of the program, on November 18, 1974. The system was checked out and shut down until December 3, 1974, when formation of dynamic membranes was undertaken. On December 10 testing with wastewater began.

The following is a list of events at Plant #50:

12/03 - Began dynamic membrane formation.

12/10 - Began parametric performance test; Selas module used. Product recycled to feed tank.

12/23 - Began parametric performance test of UOP spiral module and Westinghouse tubular module. Product water recycled to feed tank.

01/06 - Began parametric performance test of Selas modules, UOP spiral module, and Westinghouse tubular module. Reuse samples were generated.

01/10 - Began special tests.

01/13 - New Westinghouse tubular polysulfone ultrafilter installed.

01/15 - Moved to Plant #60.

01/18 - Special tests completed; last test run at Plant #60.

Procedure

The membranes for evaluation were selected based on availability and the characteristics of wastewater. The wastewater was prefiltered through 25-micron cartridge filters prior to entering the mobile laboratory. The pH was adjusted when necessary to meet membrane manufacturer specifications. Figure B-1 shows schematically the equipment arrangement. Three module types were evaluated: the dual-layer dynamic membrane on Selas[a] ceramic tubes, the spiral-wound cellulose acetate manufactured by UOP[b], and the Westinghouse[c] tubular cellulose acetate membrane.

REUSE

A sample of composite wastewater was drawn from the plant sewer, and pumped through a 25-micron filter into the mobile laboratory. The

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[a] Selas Corporation of America, Flotronics Division.

[b] Universal Oil Products, ROGA Division.

[c] Westinghouse Membrane Systems was sold to Union Carbide.

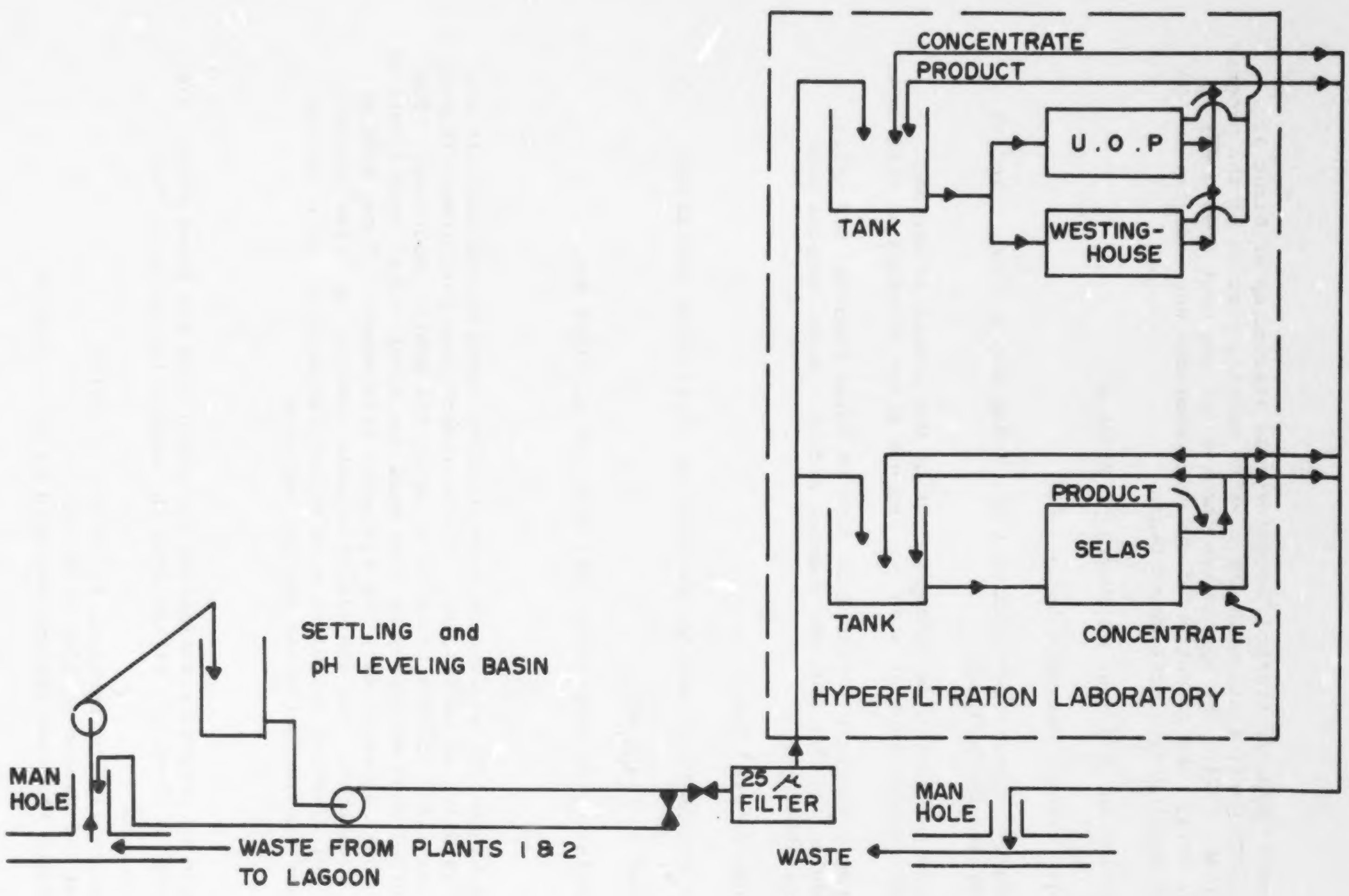
CONCENTRATE
PRODUCT
TANK
U.O.P
WESTING-HOUSE
PRODUCT
SELAS
TANK
CONCENTRATE
HYPERFILTRATION LABORATORY
SETTLING and pH LEVELING BASIN
MAN HOLE
WASTE FROM PLANTS 1 & 2 TO LAGOON
25 μ FILTER
MAN HOLE
WASTE

Figure B-1. Flow schematic for equipment set-up at Plant #50.

hyperfiltration was conducted until 90% (by volume) of the water was recovered as purified product water. Dyes, salts, etc., were concentrated in the remaining 10% of the water. Samples of both the product water and the concentrate were taken at 75% recovery and also at the 90% recovery level.

Both the 75% and the 90% recovery samples were evaluated for reuse. However, for budgetary reasons, only the 90% recovery samples were subjected to detailed chemical analyses. The 90% recovery samples, of course, represent the more severe test of reuse. Because membranes do not separate 100% of the dissolved material, the 10% by volume residue is only about eight times as concentrated as the plant composite wastewater (instead of the volumetric factor of ten).

The purified product water contains some chemicals, also because the membranes do not reject 100% of the dissolved materials. The samples of purified product water evaluated for reuse were obtained near the end of the concentration (90%), and thus contain more chemicals than the average product water would have. In fact, for these membranes the mixed product water from a full-scale hyperfiltration plant would contain only about one-third the contaminants shown by the analyses listed in Tables B-3 and B-4.

The UOP and Westinghouse membranes were tested simultaneously and therefore processed composite waste with exactly the same characteristics. The dynamic membrane was tested separately. The collection of the samples for reuse took less than three hours in the case of the cellulose acetate membranes, and about twenty hours for the dynamic membranes. In both instances, however, the concentrated residue had a high COD (5233 and 4800 mg/ℓ), was highly colored, and contained about 0.3% dissolved solids.

REUSE EVALUATION

Since the samples taken for reuse evaluation were misplaced in transit to the corporate dye laboratory, no reuse dyeings were conducted.

MEMBRANE PERFORMANCE

Three membrane performance tests were conducted. The first began on December 10, 1974, utilizing Selas modules #4, #5, and #8, with #8 being previously unexposed to a waste feed solution. During the run of approximately 200 hours, all product was recycled to the feed tank and tap water was added to make up for evaporation losses.

On December 23, a 250-hour run was begun utilizing the UOP spiral-wound cellulose acetate and a Westinghouse tubular cellulose acetate module, both run from a common feed source. During the run all product was returned to the feed tank maintaining a constant concentration. Both modules were previously exposed to other wastewater.

The final run was 70 hours in length, utilizing Selas modules #4, #5, and #1. Module #1 was previously unexposed to waste effluent. During this

TABLE B-3. CHEMICAL ANALYSES OF WATER EVALUATED FOR REUSE[a] AT PLANT #50

(90% Water Recovery)

TYPE	Selas[b] Product	Selas Concentrate
SAMPLE NUMBER	505	506
DATE TAKEN	1/7/75	1/7/75
PARAMETER[c]		
COD	84	4880
BOD	15.6	170
TOC	20	1371
Alkalinity	10	95
Hardness	<1	30
Total Solids	42	2352
Dissolved Solids	42	2276
Volatile Solids	4	1328
Color	0	2800
Turbidity	0	300
Conductivity	66	1250
Phenol	0.44	7.9
pH	7.2	6.7
Mercury	<0.01	<0.01
Manganese	0.01	0.09
Calcium	0.68	3.55
Iron	0.40	2.66
Nickel	<0.01	<0.01
Chromium	0.19	0.20
Zinc	0.08	1.44
Copper	0.1	0.20
Magnesium	0.18	1.78

[a] Reuse tests conducted in Plant #50 dye laboratory.

[b] Selas module contained ceramic tubes with dynamic membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE B-4. CHEMICAL ANALYSES OF WATER EVALUATED FOR REUSE[a] AT PLANT #50

(90% Water Recovery)

TYPE	Westinghouse[b] Product	UOP[c] Product	West/UOP Concentrate
SAMPLE NUMBER	511	513	515
DATE TAKEN	1/7/75	1/7/75	1/7/75
PARAMETER[d]			
COD	468	72	5233
BOD	24	10	285
TOC	800	22	1570
Alkalinity	50	5	390
Hardness	1	1	10
Total Solids	274	10	3250
Dissolved Solids	267	8	3182
Volatile Solids	144	4	1764
Color	180	10	2000
Turbidity	30	2	250
Conductivity	270	44	2500
Phenol	0.59	0.52	0.65
pH	6.7	6.7	7.1
Mercury	<0.01	<0.01	<0.01
Manganese	0.04	<0.01	0.12
Calcium	0.82	0.46	1.48
Iron	0.25	0.35	2.09
Nickel	<0.01	<0.01	<0.01
Chromium	0.27	<0.1	0.11
Zinc	1.41	0.10	0.88
Copper	0.1	0.1	0.12
Magnesium	0.26	0.14	0.70

[a] Reuse tests conducted in Plant #50 dye laboratory.

[b] Westinghouse module contained tubular cellulose acetate membranes.

[c] UOP module contained spiral-wound cellulose acetate membranes.

[d] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

run product and concentrate were constantly bled off in a set proportion and makeup fresh feed was added as required to maintain a constant system volume.

Three spent dye liquors were selected for consideration during the special testing portion of this program: (1) a disperse dye, (2) a basic dye, and (3) a disperse/basic dye.

The disperse dye liquor was run as received at a pH of 3.4 with the Westinghouse tubular and UOP spiral modules to 87% volumetric recovery. The waste was neutralized to ∿7 with sodium hydroxide for the Selas modules and concentrated to 86% volumetric recovery.

The basic dye was run as received at a pH of 3.8 with the UOP and Westinghouse modules and neutralized to a pH of ∿8 for the Selas modules to recoveries of 71% and 87%, respectively.

The disperse/basic dye run utilizing the Selas modules was aborted when excessive temperature of the system caused a module rupture. The disperse/basic dye was concentrated to 85% volumetric recovery utilizing the UOP and Westinghouse modules.

Samples of products and concentrates from each module and waste were provided the mill for reuse evaluation and chemical analyses.

While at Plant #50, forty-two samples were collected for chemical analyses. Of these, ten were subjected to chemical analyses by Plant #50, six were subjected to chemical analyses by Clemson University, and twenty-six were available for reuse potential tests and were analyzed by Plant #50.

Dynamic Membrane

Four modules of Selas ceramic tubes with dynamic Zr-PAA membranes were evaluated in two tests. The performance is summarized in Figures B-2 and B-3, plots of flux and rejection throughout the test periods. The characteristic initially rapid flux decline is evident. Modules #8 and #1 were not exposed to a waste stream prior to testing. Module #4 was equipped with a membrane exposed for 2000 hours operating time. This membrane exhibited higher flux and lower rejection than the newer membranes tested.

Previous experience has shown that more reliable flux decline data are obtained when the membranes are exposed to fresh feed. Therefore, the flux that would be used for design cost projections is 1.0 m/d (25 GFD) and is based on the 75-hour test when fresh feed was continuously added.

While the flux declined, the conductivity rejection increased. Both phenomena would be the result of the formation of a self-rejecting layer formed on the membrane surface from the constituents in the wastewater.

The conductivity rejection measures the separation or filtration of electrolytes by the membrane. The filtration efficiency for larger organic molecules is usually higher than for the electrolytes. Grab samples of the

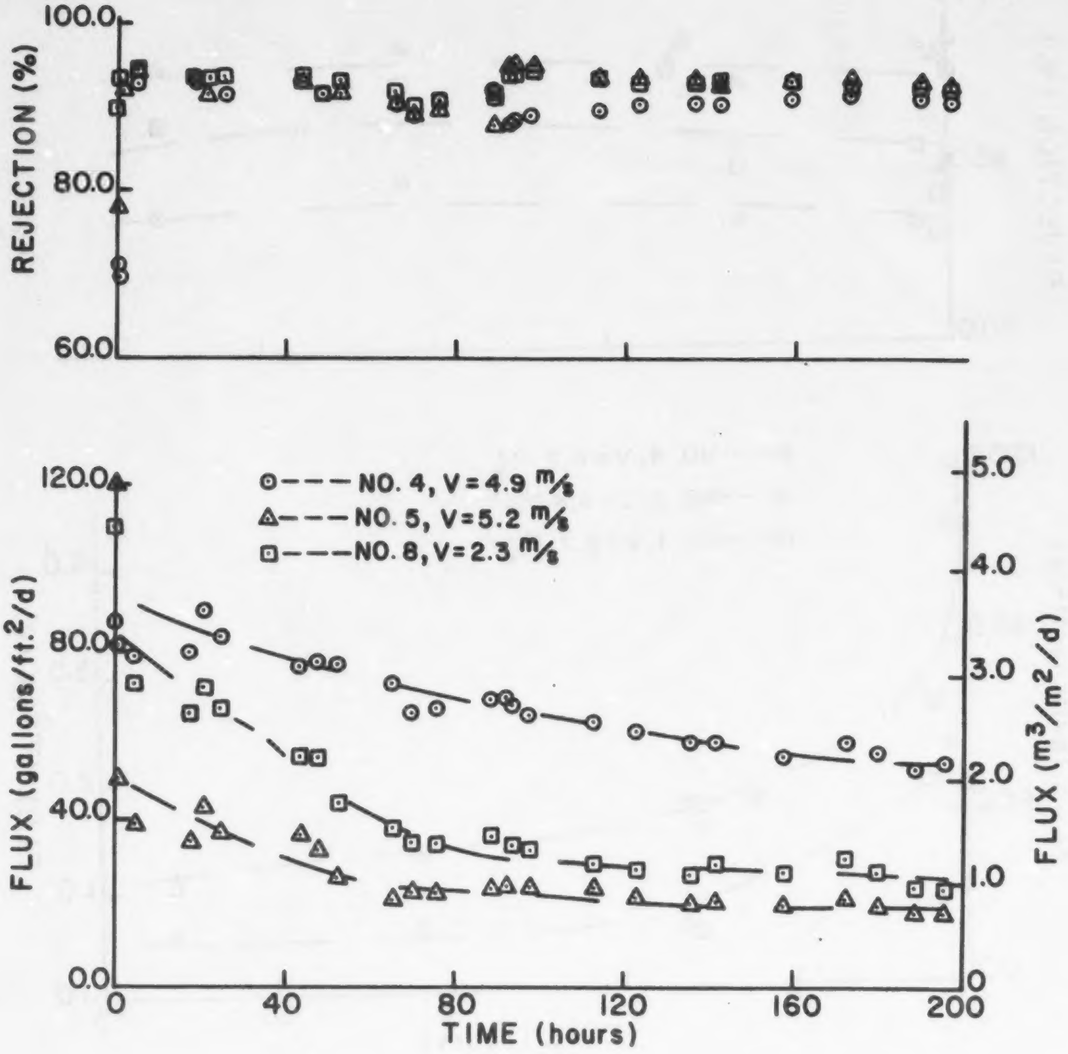

Figure B-2. Hyperfiltration of combined effluent at Plant #50 by Zr(IV)-PAA membranes on Selas ceramic supports. (P = 6.9 MPa (1000 psig); T = 60°C; pH = 6.4 - 7.8; recovery = 60%.)

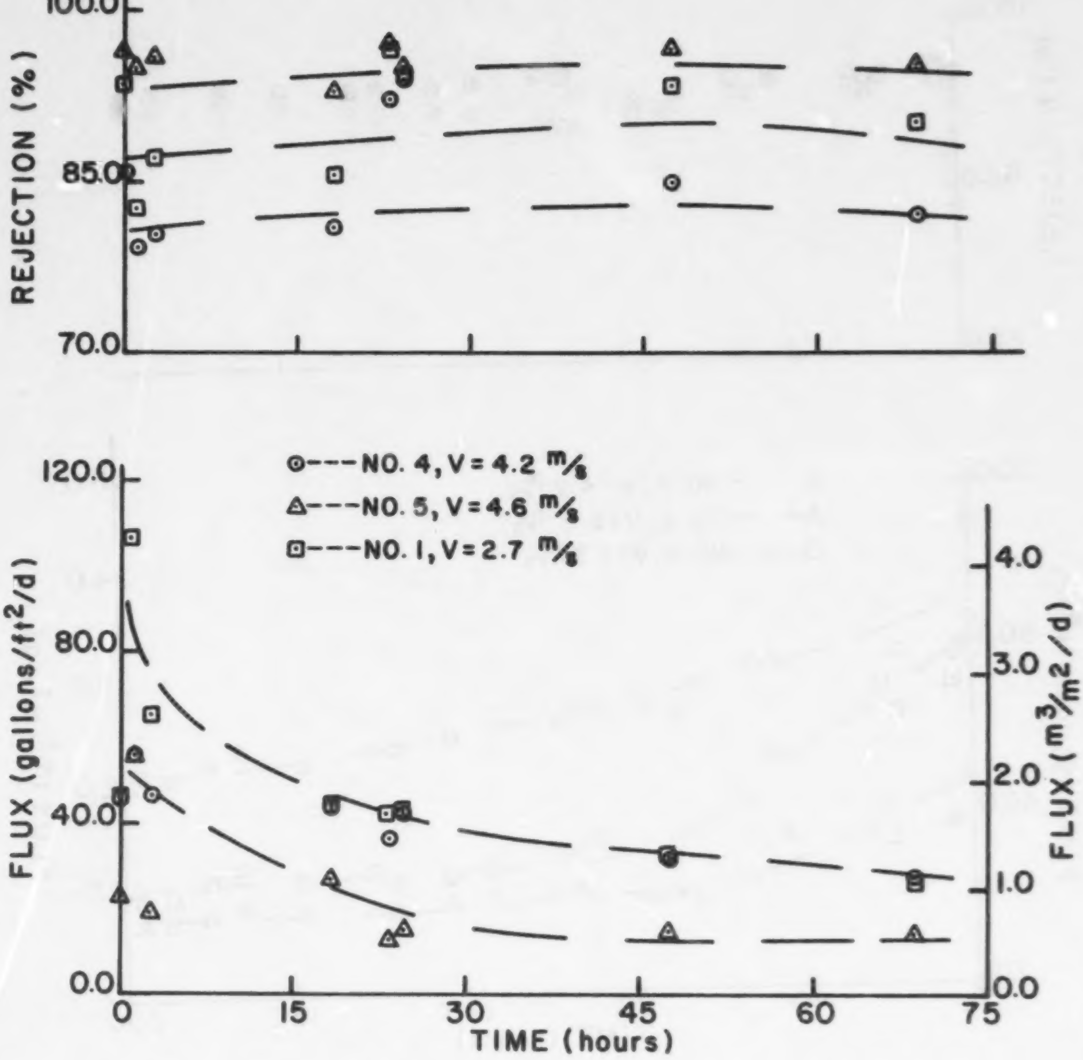

Figure B-3. Hyperfiltration of combined effluent at Plant #50 by Zr(IV)-PAA membranes on Selas ceramic supports. (P = 6.9 MPa (1000 psig); T = 54°C; pH = 5.4 - 7.6; recovery = 90%.)

feed to the membrane and the product water passing through the membranes were obtained during the 200-hour performance tests and analyzed to indicate the filtration efficiency for several constituents. The results of analyses for three pairs of samples are shown in Tables B-5, B-6, and B-7.

The 95 - 99% rejection of organics, indicated by COD, BOD, and color comparisons between the concentrate and product samples are greater than the conductivity rejections. The phenol rejection is 85 - 99%. The rejection of metals is very high, as indicated in cases where results are significantly above the limits of detection.

Cellulose Acetate Membranes

The performance of spiral-wound and tubular cellulose acetate membrane modules is summarized in Figure B-4, a plot of the flux and rejection throughout the test period. The operating conditions were as specified by the module manufacturer: 2.76 MPa (400 psig), and feed rates of 17 dm^3/min (4.5 GPM) and 13 dm^3/min (3.5 GPM) for the spiral and tubular modules, respectively. Both modules had been previously used in testing.

The flux remained near constant throughout the 200-hour test period during which time no washing procedures were attempted. All product water was recycled to the feed tank maintaining a constant feed concentration. The conductivity rejection was in the range of 90 - 95% throughout the test period. The rejection of other wastewater constituents was also very high, as indicated by the results of analyses of samples taken during the 200-hour test (see Tables B-8, B-9, and B-10). The tubular module exhibited higher flux and lower rejection than the spiral module.

TABLE B-5. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #50

SAMPLE NUMBER	516	517
TYPE	Product	Concentrate
DATE TAKEN	1/8/75	1/8/75
PARAMETER[b]		
COD	70	4633
BOD	28	820
TOC	-	-
Alkalinity	43	263
Hardness	-	-
Total Solids	156	2270
Dissolved Solids	155	2217
Volatile Solids	-	-
Color	-	-
Turbidity	0.3	120
Conductivity	170	1500
Phenol	0.086	1.130
pH	6.2	6.6
Mercury	-	-
Manganese	-	-
Calcium	-	-
Iron	0.05	2.44
Nickel	0.08	0.29
Chromium	0.08	0.09
Zinc	0.001	0.769
Copper	0.12	0.37
Magnesium	-	-

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[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

TABLE B-6. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #50

SAMPLE NUMBER	521	522
TYPE	Product	Concentrate
DATE TAKEN	1/9/75	1/9/75
PARAMETER[b]		
COD	0	5756
BOD	24	820
TOC	-	-
Alkalinity	63	340
Hardness	-	-
Total Solids	176	2640
Dissolved Solids	176	2585
Volatile Solids	-	-
Color	-	-
Turbidity	0.3	160
Conductivity	220	1700
Phenol	0	1.255
pH	6.6	6.6
Mercury	-	-
Manganese	-	-
Calcium	-	-
Iron	0.03	3.50
Nickel	0.02	0.25
Chromium	0.08	0.10
Zinc	0.004	1.476
Copper	0.10	0.34
Magnesium	-	-

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[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (NTU), conductivity (µmho/cm), and pH (unitless).

TABLE B-7. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #50

SAMPLE NUMBER	501	502
TYPE	Product	Concentrate
DATE TAKEN	1/17/75	1/17/75
PARAMETER[b]		
COD	76	912
BOD	21	150
TOC	-	-
Alkalinity	4	90
Hardness	-	-
Total Solids	253	756
Dissolved Solids	251	664
Volatile Solids	-	-
Color	-	-
Turbidity	0.7	22
Conductivity	90	6100
Phenol	0.008	0.052
pH	6.0	6.3
Mercury	-	-
Manganese	-	-
Calcium	-	-
Iron	0.03	1.04
Nickel	0	0.01
Chromium	0.07	0.09
Zinc	0.08	0.218
Copper	0.07	0.15
Magnesium	-	-

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

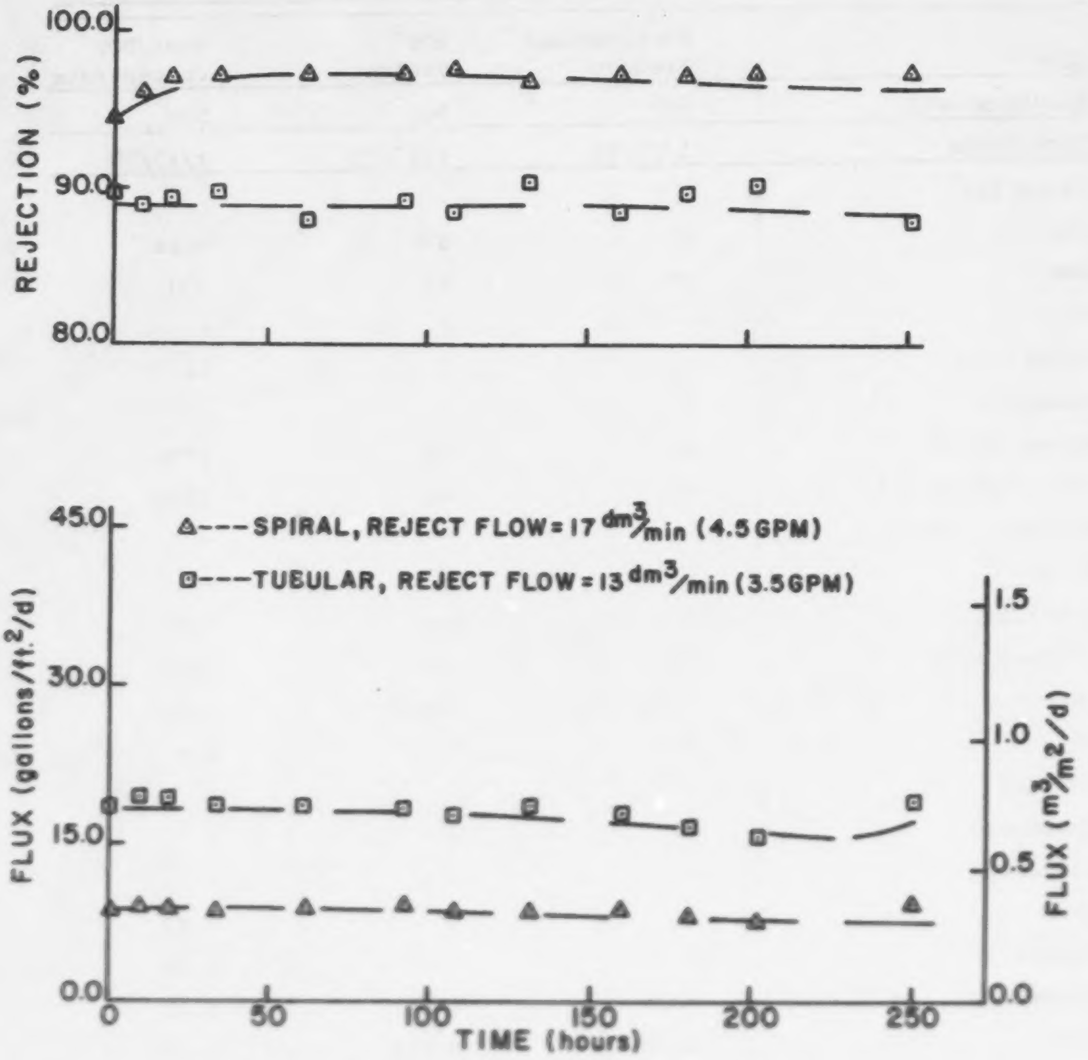

Figure B-4. Hyperfiltration of combined effluent at Plant #50 by tubular Westinghouse and spiral-wound UOP cellulose acetate membrane modules. (P = 2.8 MPa (400 psig); T = 24°C; pH = 6.9 - 7.4; recovery = 50% and 75% before and after 125 hours.)

TABLE B-8. PERFORMANCE PARAMETERS OF WESTINGHOUSE AND UOP MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #50

TYPE	Westinghouse[a] Product	UOP[b] Product	West/UOP Concentrate
SAMPLE NUMBER	507	508	509
DATE TAKEN	1/17/75	1/17/75	1/17/75
PARAMETER[c]			
COD	0	456	8664
BOD	30	25	300
TOC	-	-	-
Alkalinity	10	5	94
Hardness	-	-	-
Total Solids	82	48	1990
Dissolved Solids	82	48	1990
Volatile Solids	-	-	-
Color	-	-	-
Turbidity	0.2	0.6	0.5
Conductivity	400	82	2800
Phenol	0.010	0.008	0.020
pH	6.4	5.6	6.9
Mercury	-	-	-
Manganese	-	-	-
Calcium	-	-	-
Iron	0	0	0.13
Nickel	0	0.01	0.18
Chromium	0.09	0.08	0.10
Zinc	0.024	0.015	0.165
Copper	0.10	0.08	0.13
Magnesium	-	-	-

[a] Westinghouse module contained tubular cellulose acetate membranes.

[b] UOP module contained spiral-wound cellulose acetate membranes.

[c] All results are in mg/l, except for color (Pt-Co units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

TABLE B-9. PERFORMANCE PARAMETERS OF UOP AND WESTINGHOUSE MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #50

TYPE	UOP[a] Product	Westinghouse[b] Product	UOP/West Concentrate
SAMPLE NUMBER	518	519	520
DATE TAKEN	1/8/75	1/8/75	1/8/75
PARAMETER[c]			
COD	0	281	2738
BOD	29	58	730
TOC	-	-	-
Alkalinity	8	57	399
Hardness	-	-	-
Total Solids	96	400	1760
Dissolved Solids	96	393	1745
Volatile Solids	-	-	-
Color	-	-	-
Turbidity	0.6	11	126
Conductivity	46	250	1600
Phenol	0.012	0.005	0.540
pH	5.4	6.0	6.8
Mercury	-	-	-
Manganese	-	-	-
Calcium	-	-	-
Iron	0.13	0.10	0.93
Nickel	0.03	0.12	0.26
Chromium	0.07	0.08	0.12
Zinc	0.004	0.019	0.255
Copper	0.09	0.10	0.25
Magnesium	-	-	-

[a] UOP module contained spiral-wound cellulose acetate membranes.

[b] Westinghouse module contained tubular cellulose acetate membranes.

[c] All results are in mg/l, except for color (Pt-Co units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

TABLE B-10. PERFORMANCE PARAMETERS OF WESTINGHOUSE AND UOP MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #50

TYPE	Westinghouse[a] Product	UOP[b] Product	West/UOP Concentrate
SAMPLE NUMBER	523	524	525
DATE TAKEN	1/9/75	1/9/75	1/9/75
PARAMETER[c]			
COD	281	0	2457
BOD	35	20	275
TOC	-	-	-
Alkalinity	59	8	495
Hardness	-	-	-
Total Solids	340	28	1820
Dissolved Solids	335	28	1808
Volatile Solids	-	-	-
Color	-	-	-
Turbidity	8	0.2	40
Conductivity	290	38	1650
Phenol	0.548	0.078	0.149
pH	6.2	5.6	6.9
Mercury	-	-	-
Manganese	-	-	-
Calcium	-	-	-
Iron	0.23	0.01	1
Nickel	0.15	0	0.25
Chromium	0.09	0.09	0.12
Zinc	0.006	0.016	3.680
Copper	0.12	0.09	0.23
Magnesium	-	-	-

[a] Westinghouse module contained tubular cellulose acetate membranes.

[b] UOP module contained spiral-wound cellulose acetate membranes.

[c] All results are in mg/l, except for color (Pt-Co units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

APPENDIX C

PLANT #60

The on-site tests conducted from January 15, 1975, to February 26, 1975, were to obtain the following information: (1) plant laboratory evaluation of reuse, and (2) engineering performance data with membranes. Reuse of both the purified product and the concentrated residue was evaluated in laboratory tests conducted by Plant #60 personnel. Samples of wastewater, purified product water, and concentrated residue were analyzed by Nardin Laboratory.[a] In addition, the treatability of the concentrated residue was evaluated in bench-scale tests, Appendix J.

FIBERS AND CHEMICALS

The dyeing and finishing processes at Plant #60 involve several different dyes and finishes. The dyeing is done in atmospheric becks. The principal dyes employed, comprising 95% of the total usage, are acid, premetallized, and disperse dyes. The materials processed are acrylic (10%), nylon (80%), and polyester (10%).

Ninety percent of the 2724 m^3/d (720,000 gallons/day) total water usage was in the dyehouse. Allowing for evaporation in the dyehouse, the composite waste stream was about 95% by volume dyehouse wastewater.

WASTEWATER CHARACTERISTICS

The variety of dyes and scouring chemicals used produce a complex and variable waste stream composition. The wastewater characteristics, based on a monthly average for the summer of 1974, of plant wastewater discharge parameters are: $BOD_5 = 125$ mg/ℓ; COD = 1070 mg/ℓ; total suspended solids = 46 mg/ℓ; total dissolved solids = 552 mg/ℓ; pH = 6.1; temperature = 100°F. Tables C-1, C-2, C-3, and C-4 present the results of analyses for twelve grab samples obtained during the period of on-site testing. Plant #60 is classified as Subcategory 6, carpet mill.[b]

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[a] Division of Commonwealth Laboratory, Inc., Greenville, SC.

[b] Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Textile Point Source Category. EPA-440/1-74-022-a, US Environmental Protection Agency, Washington, DC, 1974.

TABLE C-1. CHEMICAL ANALYSES OF PLANT #60 WASTEWATER[a]

SAMPLE NUMBER	544	545	551
DATE TAKEN	1/20/75	1/20/75	1/27/75
PARAMETER[b]			
COD	837	680	760
BOD	64	50	64
TOC	172	121	122
Alkalinity	48	37	45
Hardness	2	2	0.3
Total Solids	442	396	414
Dissolved Solids	426	365	366
Volatile Solids	282	258	258
Color	30	60	50
Turbidity	65	35	40
Conductivity	245	210	219
Phenol	0.07	0.06	0.04
pH	6.7	6.2	6.4
Mercury	0.001	0.001	0.001
Manganese	0.17	0.07	0.01
Calcium	2.63	2.76	0.76
Iron	0.67	0.98	1.08
Nickel	0.1	0.16	0.18
Chromium	0.1	0.1	0.1
Zinc	0.31	0.46	0.51
Copper	0.1	0.11	0.1
Magnesium	1.6	1.87	1.82

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE C-2. CHEMICAL ANALYSES OF PLANT #60 WASTEWATER[a]

SAMPLE NUMBER	552	553	554
DATE TAKEN	1/27/75	1/22/75	1/28/75
PARAMETER[b]			
COD	845	653	447
BOD	136	24	76
TOC	137	142	100
Alkalinity	20	42	30
Hardness	5	2	3
Total Solids	394	416	318
Dissolved Solids	328	396	274
Volatile Solids	316	288	224
Color	110	80	190
Turbidity	60	30	60
Conductivity	95	217	140
Phenol	0.02	0.01	0.10
pH	5.9	6.7	6.3
Mercury	0.001	0.001	0.001
Manganese	0.13	0.13	0.08
Calcium	0.87	0.63	0.71
Iron	3.42	2.04	1.56
Nickel	0.1	0.1	0.1
Chromium	0.1	0.1	0.1
Zinc	0.23	0.33	0.23
Copper	0.15	0.11	0.35
Magnesium	2.03	2.85	2.45

[a] Grab samples of total plant effluent.

[b] All results as in mg/l, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE C-3. CHEMICAL ANALYSES OF PLANT #60 WASTEWATER[a]

SAMPLE NUMBER	555	566	572
DATE TAKEN	1/29/75	2/10/75	2/11/75
PARAMETER[b]			
COD	1140	1270	1455
BOD	220	92	240
TOC	235	287	355
Alkalinity	-33	61	20
Hardness	6	4	4
Total Solids	804	710	860
Dissolved Solids	759	680	784
Volatile Solids	420	364	622
Color	180	100	400
Turbidity	90	60	90
Conductivity	850	460	400
Phenol	0.05	0.05	0.02
pH	4.2	6.6	6.0
Mercury	0.001	0.001	0.001
Manganese	0.33	0.14	0.15
Calcium	0.42	0.44	4.09
Iron	2.75	1.79	1.73
Nickel	0.1	0.1	0.1
Chromium	0.1	0.1	0.1
Zinc	0.79	1.22	0.19
Copper	0.58	0.22	0.20
Magnesium	3.92	2.73	3.58

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (µmho/cm), and pH (unitless).

TABLE C-4. CHEMICAL ANALYSES OF PLANT #60 WASTEWATER[a]

SAMPLE NUMBER	573	580	593
DATE TAKEN	2/12/75	2/13/75	2/17/75
PARAMETER[b]			
COD	950	943	2870
BOD	160	100	275
TOC	177	180	620
Alkalinity	28	15	40
Hardness	9	3	2
Total Solids	802	430	1154
Dissolved Solids	757	386	1108
Volatile Solids	368	306	1046
Color	210	100	1150
Turbidity	50	110	110
Conductivity	595	160	140
Phenol	0.05	0.06	0.17
pH	5.8	6.2	6.6
Mercury	0.001	0.001	0.001
Manganese	0.15	0.11	0.15
Calcium	4.09	3.16	2.69
Iron	1.79	0.85	0.62
Nickel	0.1	0.1	0.1
Chromium	0.1	0.1	0.1
Zinc	0.77	0.12	0.17
Copper	0.13	0.1	0.16
Magnesium	2.84	1.92	2.54

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (µmho/cm), and pH (unitless).

SCHEDULE AND PROCEDURE

Schedule

The mobile laboratory arrived at Plant #60 on January 15, 1975. The utilities were connected and the system was placed in operation on January 20.

Initially, one-gallon (3.8ℓ) samples of purified product and concentrate were collected for reuse evaluation in the plant laboratory. A 38ℓ sample of concentrate was later collected for the biological treatability study.

The following is a list of events at Plant #60:

01/15 - Arrived from Plant #50.

01/20 - Checked UOP spiral, Westinghouse tubular, and Selas bundles.

01/21 - Began parametric performance test with daily addition of fresh feed. Selas, UOP, and Westinghouse cellulose acetate modules were used.

01/23 - Samples for reuse evaluation at 75% recovery were generated.

01/29 - Samples for reuse evaluation at 92% recovery were generated.

02/10 - Began parametric performance test with continuous addition of fresh feed.

02/17 - Began special tests of selected spent dye liquors taken from the becks. Selas and UOP modules used.

02/18 - Cleaned system and formed Zr-PAA membranes on Selas modules.

02/24 - Ended membrane formation.

02/26 - Moved to Plant #70.

Procedure

The membranes for evaluation were selected based on availability and the characteristics of wastewater. The wastewater was prefiltered through 25-micron cartridge filters prior to entering the mobile laboratory. The pH was adjusted when necessary to meet membrane manufacturer specification. Figure C-1 shows schematically the equipment arrangement. Three module types were evaluated: the dual-layer dynamic membrane on Selas[a] ceramic tubes, the spiral-wound cellulose acetate manufactured by UOP[b], and the tubular cellulose acetate module by Westinghouse.[c]

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[a] Selas Corporation of America, Flotronics Division.
[b] Universal Oil Products, ROGA Division.
[c] Westinghouse Membrane Systems was sold to Union Carbide.

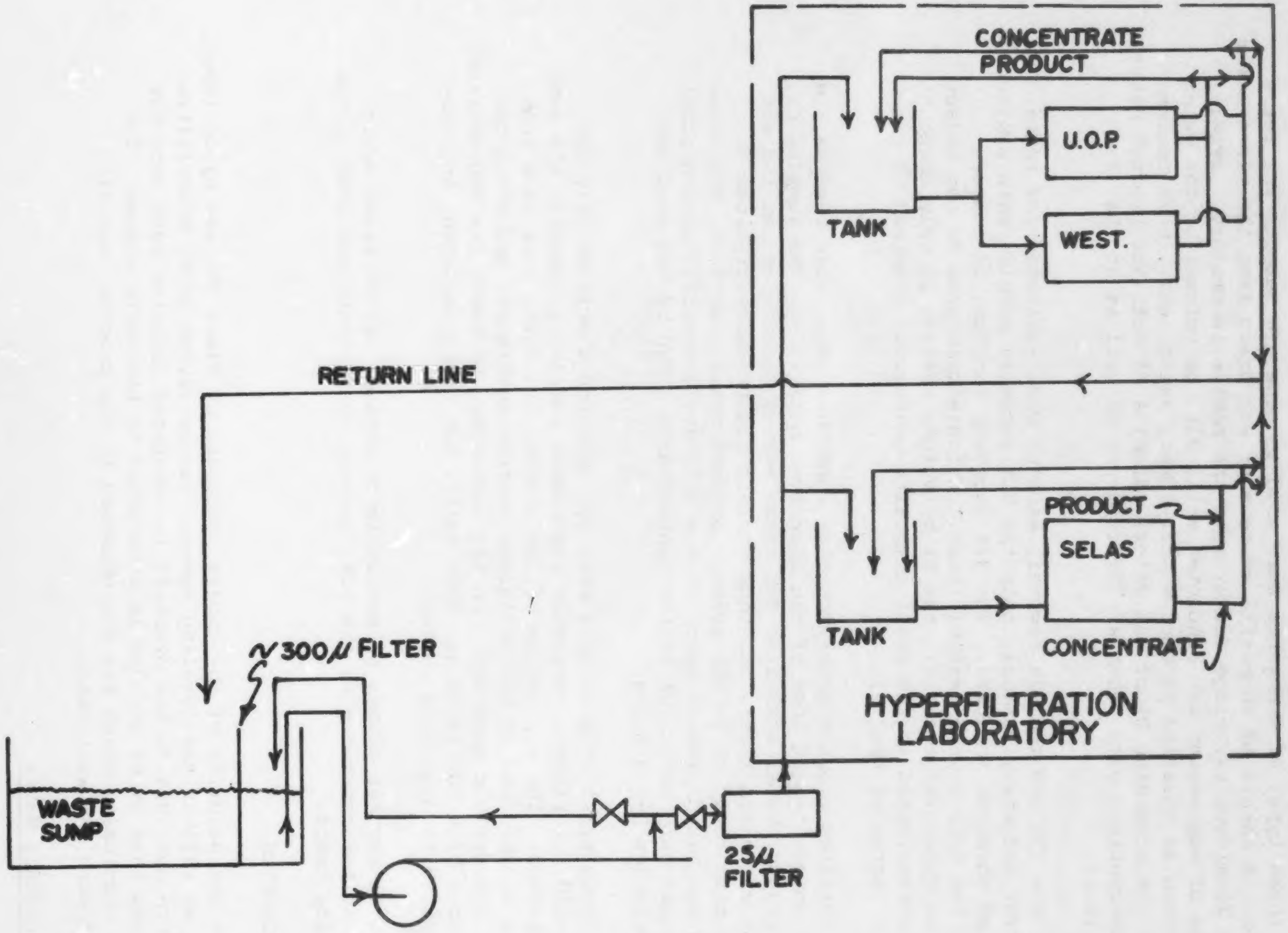
CONCENTRATE
PRODUCT
TANK
U.O.P.
WEST.
RETURN LINE
PRODUCT
SELAS
TANK
CONCENTRATE
HYPERFILTRATION LABORATORY
~300µ FILTER
WASTE SUMP
25µ FILTER

Figure C-1. Flow schematic for equipment set-up at Plant #60.

REUSE

All three types of membranes were used to generate samples for reuse evaluation. A sample of composite wastewater was drawn from the plant sewer through a 25-micron cartridge filter into the mobile laboratory. Hyperfiltration of wastewater was conducted until 92% (by volume) of the water was recovered as purified product water. Dyes, salts, etc., were concentrated in the remaining 8% of the water. Samples of both the product water and the concentrate were taken at 75% recovery as well as at the 92% recovery level.

Both the 75% and the 92% recovery samples were evaluated for reuse. However, for budgetary reasons, only the 92% recovery samples were subjected to detailed chemical analyses. The 92% recovery samples, of course, represent the more severe test of reuse. Because membranes do not reject 100% of the dissolved material, the 8% by volume residue is only about ten times as concentrated as the plant composite wastewater (instead of the volumetric factor of twelve).

The purified product water contains some chemicals, also because the membranes do not reject 100% of the dissolved materials. The samples of purified product water evaluated for reuse were obtained just at the end of the concentration (92%), and thus contain higher concentrations of chemicals than would be in the average product water. In fact, for these membranes the mixed product water from a full-scale hyperfiltration plant would contain only about 33% of the contaminants shown by the analyses listed in Tables C-5 and C-6.

The three types of membranes were not operated simultaneously and therefore did not process composite wastewater samples of exactly the same characteristics. The collection of the samples for reuse took less than five hours in the case of the cellulose acetate membranes, and about ten hours for the dynamic membrane. In all instances, however, the concentrated residue had a high COD (4560 and 7650 mg/ℓ), was highly colored, and contained about 0.5% dissolved solids.

Since it may not always be desirable to attempt direct reuse or reclamation of the concentrate, the 92% recovery concentrate was used in the treatability tests.

REUSE EVALUATION

Since the majority of the fibers processed by Plant #60 are nylon (80%), the dyes, as well as the leveling agents, can be reused after hyperfiltration. Since over 95% of the dyestuff is exhausted from the bath onto the fibers, less than 5% of the dye is discharged to the waste stream. The auxiliary chemicals, which are not consumed in the process, are all discharged with the wastewater.

Reuse of Product Water

As a stringent test of the reuse of the product water, the 92% recovery

TABLE C-5. CHEMICAL ANALYSES OF WATER EVALUATED FOR REUSE[a] AT PLANT #60

(92% Water Recovery)

TYPE	Selas[b] Product	Selas Concentrate
SAMPLE NUMBER	561	562
DATE TAKEN	1/29/75	1/29/75
PARAMETER[c]		
COD	120	4560
BOD	2.1	66
TOC	28	1457
Alkalinity	19	70
Hardness	<1	14
Total Solids	62	3148
Dissolved Solids	62	3109
Volatile Solids	18	2138
Color	10	1800
Turbidity	0	100
Conductivity	55	1000
Phenol	0.03	0.02
pH	6.8	6.4
Mercury	<0.01	<0.01
Manganese	0.03	0.30
Calcium	0.55	1.42
Iron	0.47	0.94
Nickel	<0.01	0.06
Chromium	-	-
Zinc	-	-
Copper	<0.1	0.11
Magnesium	0.15	1.03

[a] Reuse tests conducted in Plant #60 dye laboratory.

[b] Selas module contained ceramic tubes with dynamic membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE C-6. CHEMICAL ANALYSES OF WATER EVALUATED FOR REUSE[a] AT PLANT #60
(92% Water Recovery)

TYPE	UOP[b] Product	Westinghouse[c] Product	UOP/West Concentrate
SAMPLE NUMBER	563	564	565
DATE TAKEN	1/29/75	1/29/75	1/29/75
PARAMETER[d]			
COD	64	284	7650
BOD	5	14	1800
TOC	13	63	1800
Alkalinity	10	5	160
Hardness	<1	3	50
Total Solids	10	186	6314
Dissolved Solids	10	181	6303
Volatile Solids	4	80	3504
Color	8	40	1500
Turbidity	2	10	60
Conductivity	37	140	2700
Phenol	0	0.03	0
pH	6.5	5.6	5.8
Mercury	<0.01	<0.01	<0.01
Manganese	0.01	<0.01	1.32
Calcium	0.38	0.66	3.77
Iron	0.27	0.30	8.48
Nickel	<0.01	<0.01	<0.01
Chromium	-	-	-
Zinc	-	-	-
Copper	<0.1	0.1	0.50
Magnesium	0.11	0.11	1.30

[a] Reuse tests conducted in Plant #60 dye laboratory.

[b] UOP module contained spiral-wound cellulose acetate membranes.

[c] Westinghouse module contained tubular cellulose acetate membranes.

[d] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

samples were evaluated. The analyses of the product water indicates that, in general, the COD and dissolved solids are more than expected for tap water, but the concentration of metals is less.

All of the purified product water generated by the mobile laboratory at Plant #60 was suitable for reuse. Two dyeings, including tricolor carpet shades, were conducted by the plant laboratory using the product water.

The first was Amber Red on polyester fabric using the dyes: Disperse Yellow Three, Cerise Y, Disperse Blue 87, Pat-Level-40, Kelate 100, and Antifoam J-S. The second was Golden Touch Tricolor on polyester/nylon blend fabric using the dyes: Basic Yellow 53, Basic Red 17, Basic Blue 22, Disperse Blue 87, Acid Yellow 135, Acid Red 266, Pat-Level-40, Antifoam, and metasodium phosphate.

The dyeing procedure for these tests was:

(1) Add dyes and leveling agents to bath.
(2) Add carpet swatch and bring to boil over thirty minutes.
(3) Boil for thirty minutes to one hour.
(4) Rinse in cold water and dry.

Reuse of Concentrate

The attempts by the laboratory to use the concentrate in standard production procedures had limited success. The composite waste contained a complex mixture of dyes which could only be reused to dye a dull or dark shade.

It may be possible, when the wastewater and chemicals are recycled, to change the process to (1) achieve faster dyeing cycles, and/or (2) to eliminate the need for some auxiliary chemicals. For example, with direct dyeing of cellulose, salt can be eliminated by using higher concentrations of dye in the dyebath. Excess dyestuffs can be recovered by the membranes for reuse in the next cycle. Depending on the amount of fiber dyed and range of colors, this modification may or may not be practical. Water, chemicals, and energy requirements will play a major role in the selection of dyeing processes used in the future.

MEMBRANE PERFORMANCE

Universal Oil Product and Westinghouse cellulose acetate modules, and Selas dynamic Zr-PAA membrane modules, were operated on prefiltered (no pH adjustment was necessary) composite wastewater in two tests of 110 and 340 hours. During the 340-hour test, fresh feed was added on a daily basis after which sufficient quantities of product and concentrate were discarded to maintain a prescribed recovery. During the 110-hour test, fresh feed was added and product and concentrate were discarded on a continuous basis. The performance of the membranes was monitored by periodic measurements of the product water flow rate through the membranes and the percentage conductivity rejection.

The two cellulose acetate modules and the Zr-PAA modules were fed from separate feed tanks so that high-temperature operation of the Zr-PAA membranes would be possible.

Dynamic Membrane

Two modules of Selas ceramic tubes with dynamic Zr-PAA membranes were evaluated. The performance is summarized in Figures C-2 and C-3, graphs of flux and rejection throughout the test periods. The characteristic initially rapid flux decline is evident. One of the modules, #6, was equipped with new membranes and therefore had a higher initial flux. Module #5 was equipped with membranes that had already been used at Plant #50. This older membrane exhibited a lower initial flux.

The effect of fluid velocity on the flux decline was the subject of parametric testing. The lowering of the velocity of #5 and raising the velocity of #6 at the 240-hour point (see Figure C-2) showed little effect on the flux decline rate. The flux that would be used for design cost projections is 0.8 m/d (20 gallons/ft^2/d) at 50°C and 6.8 MPa (1000 psig), a value of only about 30% of the initial flux.

The conductivity rejection allows measurement of the electrolyte filtration by the membrane. The filtration efficiency for larger organic molecules is usually higher than for the electrolytes. Grab samples of the feed to the membrane and the product water passing through the membranes were obtained during the performance tests and analyzed to indicate the filtration efficiency for several constituents. The results of analyses for four pairs of samples are shown in Tables C-7 through C-10.

The 95 - 99% rejection of organics, indicated by COD, BOD, and color comparisons between the concentrate and product samples are greater than the conductivity rejections. The rejection of metals is very high, as indicated in cases where results are significantly above the limit of detection.

Cellulose Acetate Membranes

The performance of spiral-wound and tubular cellulose acetate membrane modules is summarized in Figures C-4 and C-5, graphs of the flux and rejection throughout the test periods. The operating conditions were as specified by the module manufacturers: 2.76 MPa (400 psig), and feed rates of 14 - 15 dm^3/min (3.5 - 4 GPM), and 12 dm^3/min (3.2 GPM) for the spiral and tubular, respectively.

The flux declined throughout the test periods during which time no washing procedures were attempted. The conductivity rejection was in the range of 90 - 95% for the spiral and 60 - 90% for the tubular. The rejection of other wastewater constituents was also very high, as indicated by the results of analyses of samples taken during the two tests (see Tables C-11 through C-14).

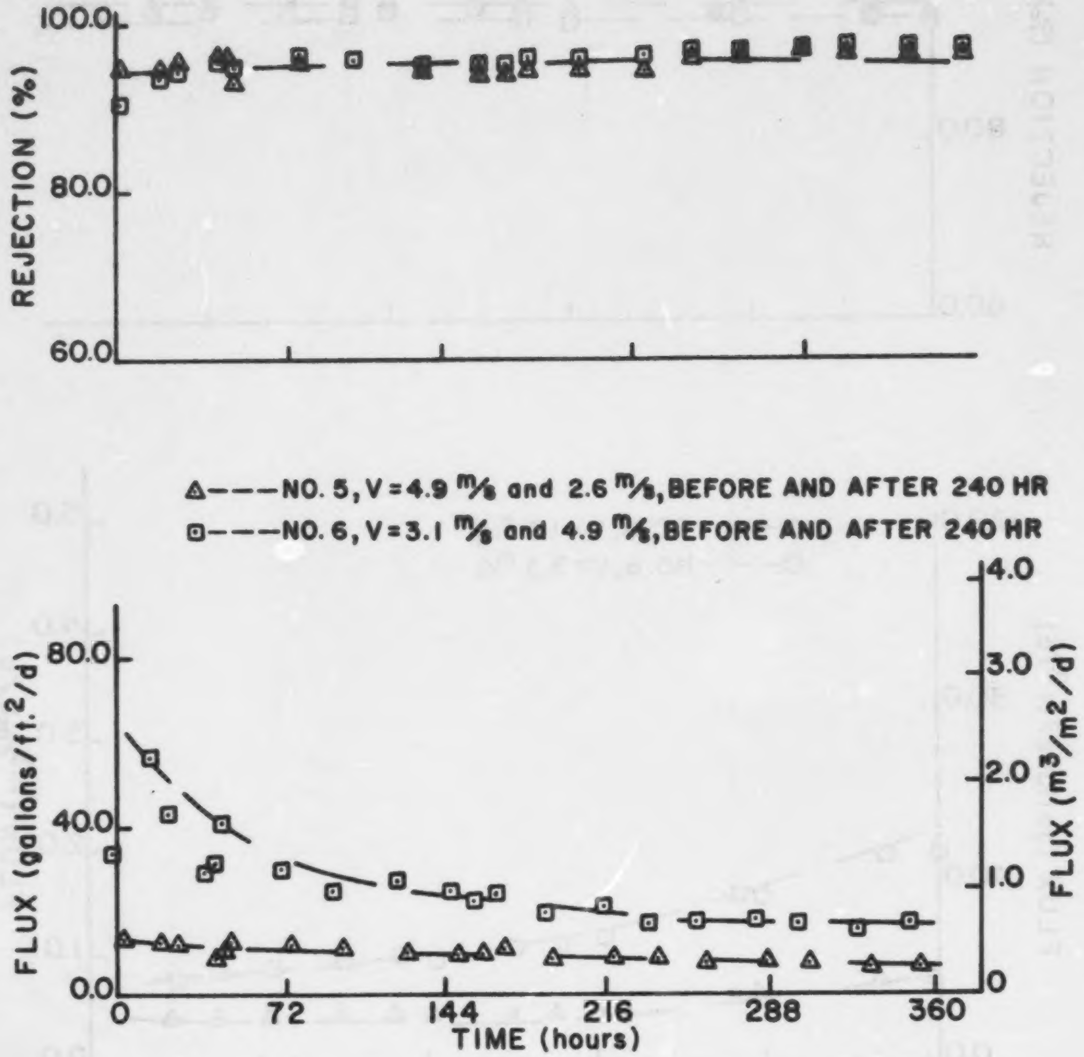

Figure C-2. Hyperfiltration of combined effluent at Plant #60 by Zr(IV)-PAA membranes on Selas ceramic supports. (P = 6.9 MPa (1000 psig); T = 50°C; pH = 6.6 - 7.2; recovery = 75%; maintained by daily addition of fresh feed and recycled product.)

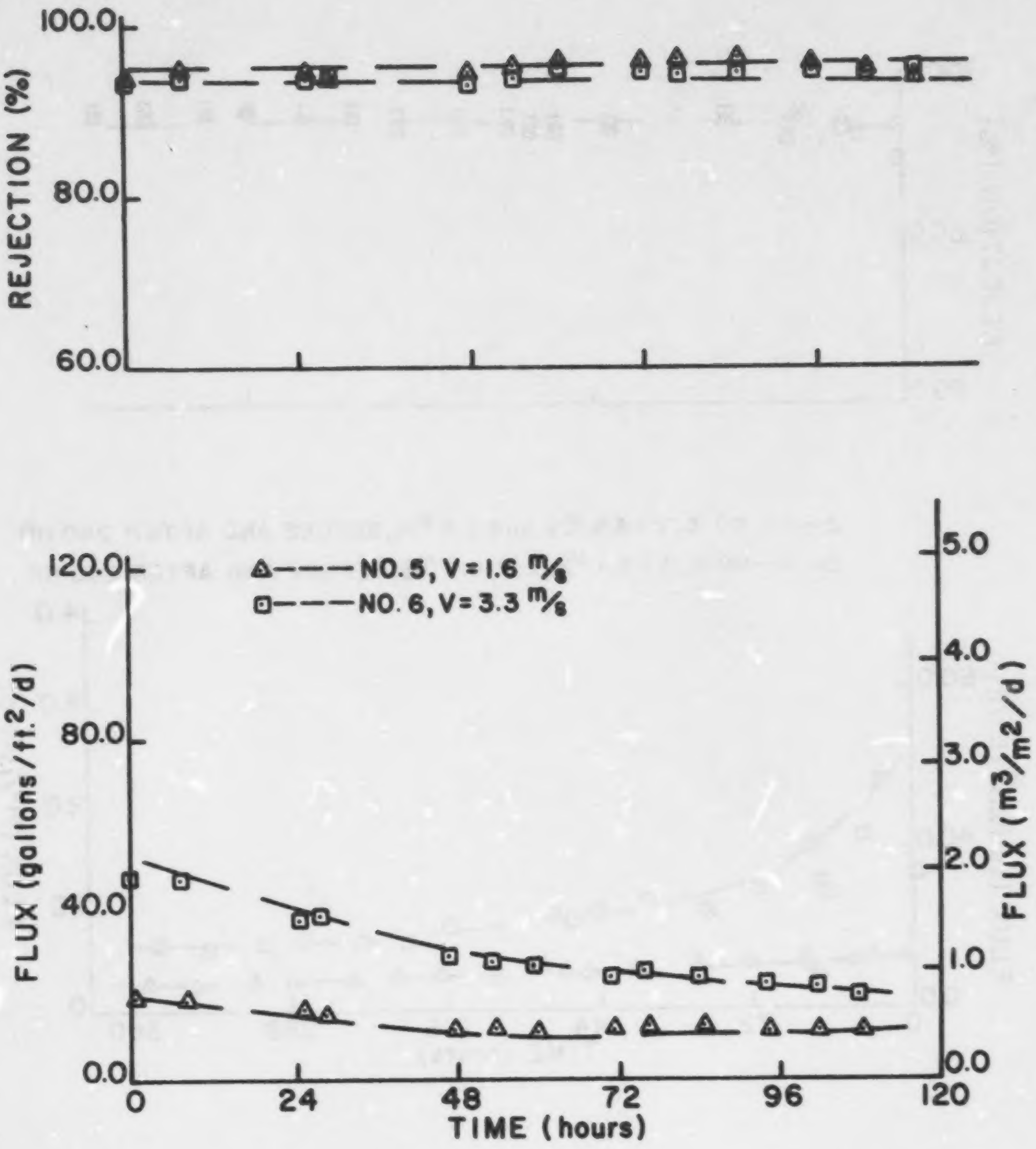

Figure C-3. Hyperfiltration of combined effluent at Plant #60 by Zr(IV)-PAA membranes on Selas ceramic supports. (P = 6.9 MPa (1000 psig); T = 61°C; pH = 6.1 - 6.9; recovery = 75%.)

TABLE C-7. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #60

SAMPLE NUMBER	567	568
TYPE	Concentrate	Product
DATE TAKEN	2/10/75	2/10/75
PARAMETER[b]		
COD	1330	69
BOD	96	6
TOC	225	42
Alkalinity	62	8
Hardness	3	0.5
Total Solids	722	30
Dissolved Solids	679	28
Volatile Solids	370	22
Color	120	0
Turbidity	40	0
Conductivity	450	30
Phenol	0	0
pH	6.6	6.4
Mercury	0.001	0.001
Manganese	0.15	0.27
Calcium	3.06	2.76
Iron	1.60	1.40
Nickel	0.1	0.1
Chromium	0.1	0.1
Zinc	1.28	0.09
Copper	0.18	0.1
Magnesium	2.36	1.25

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE C-8. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #60

SAMPLE NUMBER	574	575
TYPE	Product	Concentrate
DATE TAKEN	2/12/75	2/12/75
PARAMETER[b]		
COD	77	5270
BOD	7	380
TOC	60	1080
Alkalinity	14	58
Hardness	0.5	25
Total Solids	84	3244
Dissolved Solids	83	3205
Volatile Solids	26	2140
Color	5	1200
Turbidity	3	160
Conductivity	70	1400
Phenol	0.01	0.13
pH	6.8	6.1
Mercury	0.001	0.001
Manganese	0.02	0.65
Calcium	0.53	4.57
Iron	0.50	2.63
Nickel	0.1	1.4
Chromium	0.1	0.1
Zinc	0.1	3.04
Copper	0.1	0.28
Magnesium	1.04	7.7

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE C-9. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #60

SAMPLE NUMBER	582	583
TYPE	Product	Concentrate
DATE TAKEN	2/13/75	2/13/75
PARAMETER[b]		
COD	73	6374
BOD	6	190
TOC	62	1100
Alkalinity	15	47
Hardness	0.5	30
Total Solids	78	1782
Dissolved Solids	76	1734
Volatile Solids	14	1112
Color	5	400
Turbidity	0	300
Conductivity	80	1550
Phenol	0.05	0.16
pH	7.0	6.1
Mercury	0.001	0.001
Manganese	0.01	0.94
Calcium	0.72	3.97
Iron	0.75	4.85
Nickel	0.1	0.28
Chromium	0.1	0.24
Zinc	0.15	3.73
Copper	0.1	0.46
Magnesium	1.07	8.74

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE C-10. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #60

SAMPLE NUMBER	587	588
TYPE	Product	Concentrate
DATE TAKEN	2/14/75	2/14/75
PARAMETER[b]		
COD	134	7100
BOD	24	800
TOC	37	1380
Alkalinity	15	38
Hardness	0.5	22
Total Solids	184	3668
Dissolved Solids	171	3639
Volatile Solids	98	2270
Color	30	2000
Turbidity	15	300
Conductivity	110	1600
Phenol	0.06	0.12
pH	6.1	5.8
Mercury	0.001	0.001
Manganese	0.1	1.02
Calcium	0.76	0.84
Iron	0.44	4.79
Nickel	0.11	3.87
Chromium	0.1	0.21
Zinc	0.19	3.50
Copper	0.1	0.59
Magnesium	1.31	9.22

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

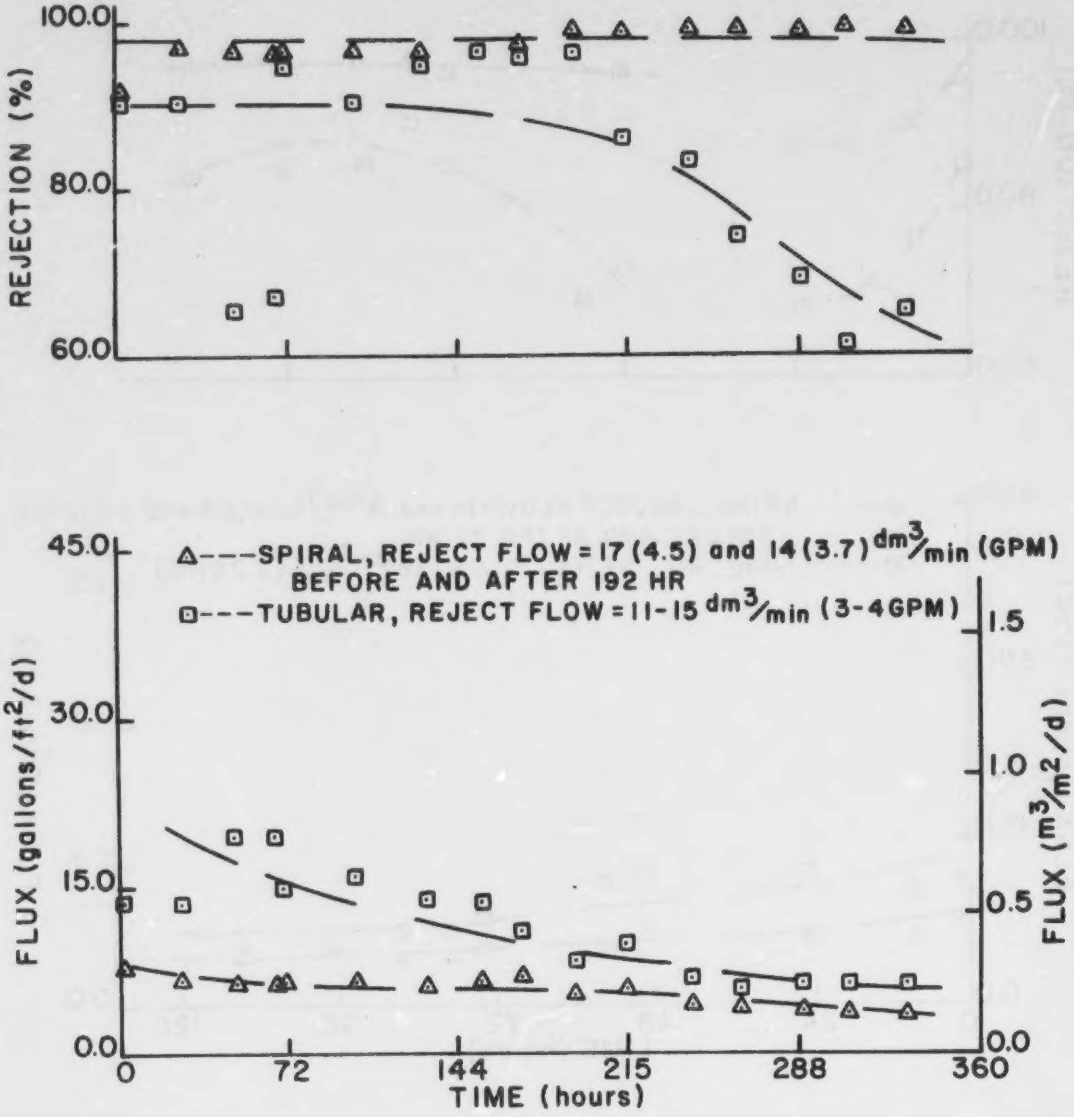

Figure C-4. Hyperfiltration of combined effluent at Plant #60 by Westinghouse tubular and UOP spiral-wound cellulose acetate membrane modules. (P = 2.8 MPa (400 psig); T = 20°C; pH = 6.4 - 7.0; recovery = 75% and 90% before and after 160 hours.)

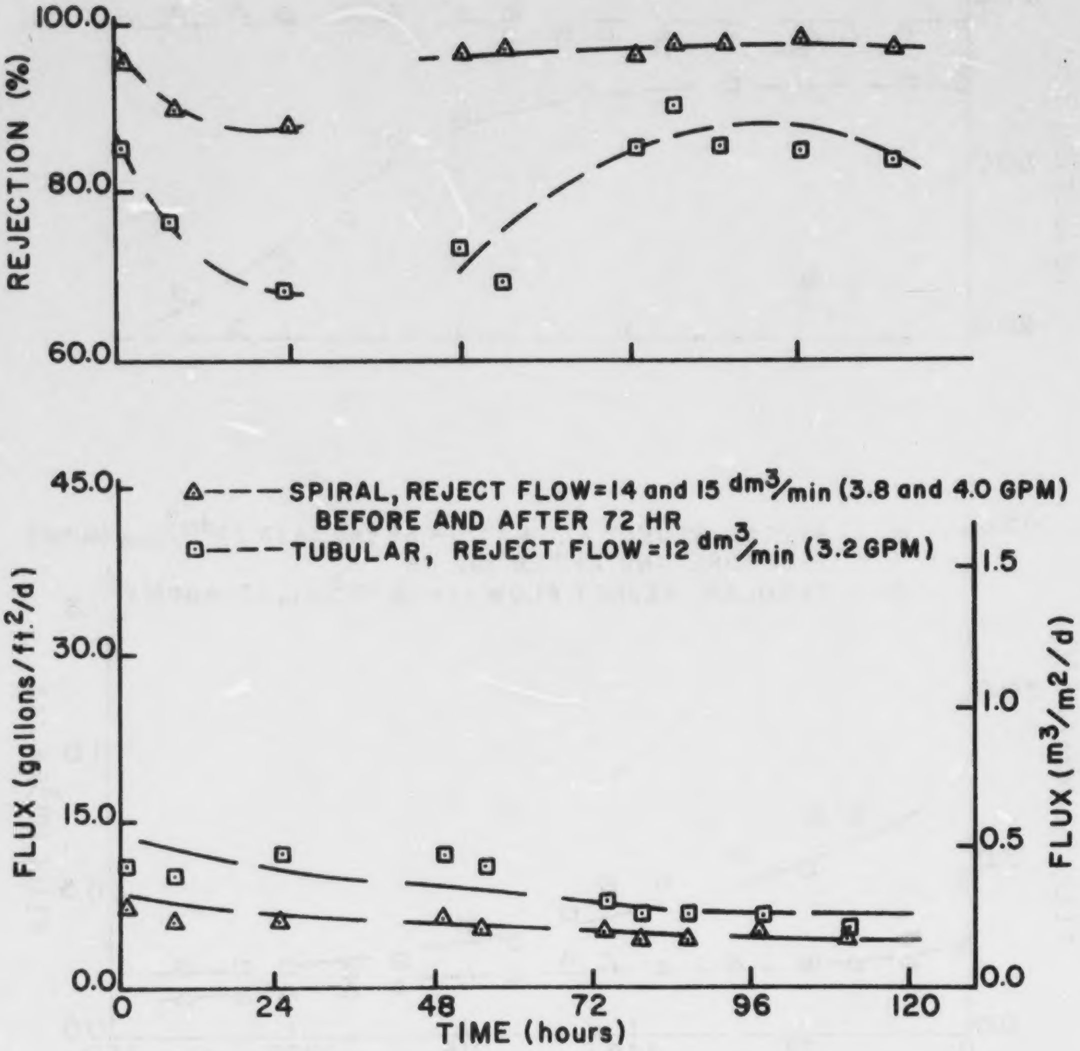

Figure C-5. Hyperfiltration of combined effluent at Plant #60 by Westinghouse tubular and UOP spiral-wound cellulose acetate membrane modules. (P = 2.8 MPa (400 psig); T = 22°C; pH = 6.4 - 6.9; recovery = 75%.)

TABLE C-11. PERFORMANCE PARAMETERS OF UOP AND WESTINGHOUSE MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #60

TYPE	UOP/West Concentrate	UOP[a] Product	Westinghouse[b] Product
SAMPLE NUMBER	569	570	571
DATE TAKEN	2/10/75	2/10/75	2/10/75
PARAMETER[c]			
COD	1765	41	126
BOD	128	9	10
TOC	345	6	31
Alkalinity	14	4	4
Hardness	4	0	1
Total Solids	710	20	72
Dissolved Solids	670	19	65
Volatile Solids	630	16	62
Color	220	0	5
Turbidity	40	0	15
Conductivity	92	6.9	19
Phenol	0.05	0	0.02
pH	6.1	5.7	5.6
Mercury	0.001	0.001	0.001
Manganese	0.02	0.07	0.17
Calcium	0.81	0.57	0.57
Iron	2.29	1.77	1.67
Nickel	0.11	0.11	0.11
Chromium	0.1	0.1	0.1
Zinc	0.21	0.07	0.1
Copper	0.14	0.11	0.1
Magnesium	3.56	2.24	1.4

[a] UOP module contained spiral-wound cellulose acetate membranes.

[b] Westinghouse module contained tubular cellulose acetate membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE C-12. PERFORMANCE PARAMETERS OF WESTINGHOUSE AND UOP MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #60

TYPE	Westinghouse[a] Product	UOP[b] Product	West/UOP Concentrate
SAMPLE NUMBER	576	577	578
DATE TAKEN	2/12/75	2/12/75	2/12/75
PARAMETER[c]			
COD	837	36	3525
BOD	124	5	250
TOC	155	6	840
Alkalinity	12	4	36
Hardness	5	1	28
Total Solids	558	12	2136
Dissolved Solids	540	12	2097
Volatile Solids	390	10	1638
Color	70	0	380
Turbidity	20	2	40
Conductivity	190	16	620
Phenol	0.01	0.02	0.02
pH	5.6	6.0	6.2
Mercury	0.001	0.001	0.001
Manganese	0.14	0.01	0.47
Calcium	0.39	0.46	0.43
Iron	1.21	0.52	3.21
Nickel	0.1	0.1	0.22
Chromium	0.1	0.1	0.1
Zinc	0.45	0.07	1.07
Copper	0.57	0.1	0.16
Magnesium	2.94	1.09	6.76

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[a] Westinghouse module contained tubular cellulose acetate membranes.

[b] UOP module contained spiral-wound cellulose acetate membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE C-13. PERFORMANCE PARAMETERS OF WESTINGHOUSE AND UOP MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #60

TYPE	Westinghouse Product	UOP Product	West/UOP Concentrate
SAMPLE NUMBER	584	585	586
DATE TAKEN	2/13/75	2/13/75	2/13/75
PARAMETER[c]			
COD	337	45	4660
BOD	8	6	290
TOC	80	94	870
Alkalinity	16	17	77
Hardness	1	0.3	10
Total Solids	188	12	2840
Dissolved Solids	176	10	2804
Volatile Solids	118	10	1976
Color	40	5	1200
Turbidity	30	5	40
Conductivity	110	39	1100
Phenol	0.02	0.04	0.11
pH	5.8	6.4	6.1
Mercury	0.001	0.001	0.001
Manganese	0.11	0.01	0.61
Calcium	0.37	0.35	0.69
Iron	2.73	0.71	3.21
Nickel	0.1	0.1	0.11
Chromium	0.28	0.1	0.1
Zinc	0.24	0.08	0.99
Copper	0.15	0.1	0.18
Magnesium	3.44	1.59	6.98

[a] Westinghouse module contained tubular cellulose acetate membranes.

[b] UOP module contained spiral-wound cellulose acetate membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE C-14. PERFORMANCE PARAMETERS OF UOP AND WESTINGHOUSE MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #60

TYPE	UOP[a] Product	Westinghouse[b] Product	UOP/West Concentrate
SAMPLE NUMBER	589	590	591
DATE TAKEN	2/14/75	2/14/75	2/14/75
PARAMETER[c]			
COD	36	219	3550
BOD	5	16	150
TOC	8	54	620
Alkalinity	3	12	48
Hardness	0.5	1	19
Total Solids	10	190	2060
Dissolved Solids	9	182	2038
Volatile Solids	2	118	1412
Color	15	70	750
Turbidity	0	10	90
Conductivity	16	91	840
Phenol	0.01	0	0.04
pH	6.4	6.2	6.2
Mercury	0.001	0.001	0.001
Manganese	0.01	0.06	0.52
Calcium	0.63	0.70	0.69
Iron	0.69	1.02	2.38
Nickel	0.1	0.22	0.13
Chromium	0.1	0.1	0.1
Zinc	0.1	0.29	0.91
Copper	0.1	0.1	0.1
Magnesium	3.92	2.48	5.77

[a] UOP module contained spiral-wound cellulose acetate membranes.

[b] Westinghouse module contained tubular cellulose acetate membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

APPENDIX D

PLANT #70

The on-site tests conducted from February 26, 1975, to March 26, 1975, were to obtain the following information: (1) plant laboratory evaluation of reuse, and (2) engineering performance data with membranes. Reuse of both the purified product water and the concentrated residue was evaluated in laboratory tests conducted by Plant #70 personnel. Samples of wastewater, purified product water, and the concentrated residue were analyzed by Nardin Laboratory.[a] In addition, the treatability of the concentrated residue was evaluated in bench-scale tests, Appendix J.

The production parameters of Plant #70, given in Table D-1, provide a basis for evaluation of the results of the project. The factors are important in the evaluation of the practicality of scale-up from the pilot plant.

FIBERS AND CHEMICALS

The dyeing and finishing processes at Plant #70 involve several different dyes and finishes. The dyeing is done in high-temperature package-dyeing machines and atmospheric skein-dyeing equipment. The principal dyes employed, comprising 95% of the total usage, are basic dyes. The materials processed are acrylic (98%), nylon (1%), and wool and mohair (1%).

Ninety percent of the 1892 m^3/d (500,000 gallons/day) total water usage is in the dyehouse. Allowing for evaporation in the dyehouse, the composite waste stream is at least 85% by volume dyehouse wastewater.

WASTEWATER CHARACTERISTICS

The variety of dyes and scouring chemicals used produce a complex and variable waste stream composition. The wastewater characteristics, based on a monthly average for the summer of 1974, of plant wastewater discharge parameters are: BOD_5 = 375 mg/ℓ; COD = 700 mg/ℓ; total suspended solids = 140 mg/ℓ; total dissolved solids = 800 mg/ℓ; pH = 4.0; temperature = 160°F. Table D-2 presents the results of analyses for two grab samples obtained

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[a] Division of Commonwealth Laboratory, Inc., Greenville, SC.

[b] Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Textile Point Source Category. EPA-440/1-022-a, US Environmental Protection Agency, Washington, DC, 1974.

TABLE D-1. PLANT #70 PRODUCTION CAPACITY PARAMETERS

QUANTITIES USED	
Materials: acrylic, nylon, wool, mohair	
Water (total to plant), m^3/day	1,892
(gallons/day)	(500,000)
Water (to dyehouse), m^3/day	1,649
(gallons/day)	(435,335)
Dyes, kg/day	250
(pounds/day)	(550)
Auxiliary Chemicals, kg/day	1,140
(pounds/day)	(2,514)
Energy (for process steam), joules/day	292×10^9
(Btu/day)	(278×10^6)
UNIT COSTS	
Water, ¢/m^3	6
(\$/1000 gallons)	(0.23)
Fuel Oil, ¢/10^7 joules	1.9
(\$/10^6 Btu)	(2.06)

TABLE D-2. CHEMICAL ANALYSES OF PLANT #70 WASTEWATER[a]

SAMPLE NUMBER	600	617
DATE TAKEN	2/28/75	3/10/75
PARAMETER[b]		
COD	226	973
BOD	135	510
TOC	-	-
Alkalinity	34	38
Hardness	8	55
Total Solids	371	723
Dissolved Solids	329	657
Volatile Solids	-	-
Color	20	500
Turbidity	2.1	6.3
Conductivity	430	540
Phenol	0.011	0.009
pH	7.25	7.50
Mercury	-	-
Manganese	-	-
Calcium	0.120	0.360
Iron	0.020	0.475
Nickel	0.067	0.100
Chromium	0.020	0.020
Zinc	0.125	4.792
Copper	0.018	3.357
Magnesium	-	-

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

during the period of on-site testing. Plant #70 is classified as Subcategory 7, stock and yarn dyeing and finishing.[a]

SCHEDULE AND PROCEDURE

Schedule

The mobile laboratory arrived at Plant #70 on February 26, 1975. The utilities were connected and the system was placed in operation on February 28.

Initially, one-gallon (3.8ℓ) samples of purified product and concentrate were collected for reuse evaluation in the plant laboratory. A 38ℓ sample of concentrate was later collected for the biological treatability study.

The following is a list of events at Plant #70:

02/26 - Arrived from Plant #60; utilities connected.

02/27 - Operated UOP module with standard salt solution (1000 mg/ℓ).

02/28 - Operated Selas modules #9, #4, and #12 with standard salt solution.

03/03 - Plant personnel replaced 5 kva transformer in mobile lab.

03/04 - Began reuse tests; feed neutralized from 4.3 to 7.1 for Selas modules. Not neutralized for UOP module.

03/07 - Began engineering performance tests; waste neutralized to ∿7 for all modules.

03/15 - Ended engineering performance tests.

03/19 - Operated Selas #9, #4 with salt solution. Began special tests with spent dye liquor.

03/21 - Ended special tests.

03/25 - Prepared for departure.

03/26 - Moved to Plant #40.

Procedure

The membranes for evaluation were selected based on availability and the characteristics of the wastewater. The wastewater was prefiltered through 25-micron cartridge filters prior to entering the mobile laboratory. The pH was adjusted when necessary to meet membrane manufacturer specifications. Figure D-1 shows schematically the equipment arrangement. Two module types were evaluated: the dual-layer dynamic membrane on Selas[a] ceramic tubes, and the spiral-wound cellulose acetate manufactured by UOP[b].

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[a] Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Textile Point Source Category. EPA-440/1-74-022-a, US Environmental Protection Agency, Washington, DC, 1974.

REUSE

Both types of membranes were used to generate samples for reuse evaluation. A sample of composite wastewater was drawn from the plant sewer, and pumped through a 25-micron filter into the mobile laboratory. The hyperfiltration was conducted until 90% (by volume) of the water was recovered as purified product water. Dyes, salts, etc., were concentrated in the remaining 10% of the water. Samples of both the product water and the concentrate were taken at 75% recovery, and also at the 90% recovery level.

Both the 75% and the 90% recovery samples were evaluated for reuse. However, for budgetary reasons, only the 90% recovery samples were subjected to detailed chemical analyses. The 90% recovery samples, of course, represent the more severe test of reuse. Because membranes do not separate 100% of the dissolved material, the 10% by volume residue is only about eight times as concentrated as the plant composite wastewater (instead of the volumetric factor of ten).

The purified product water contains some chemicals, also because the membranes do not reject 100% of the dissolved materials. The samples of purified product water evaluated for reuse were obtained near the end of the concentration (90%), and thus contain more chemicals than the average product water would have. In fact, for these membranes the mixed product water from a full-scale hyperfiltration plant would contain only about one-third the contaminants shown by the analyses listed in Tables D-3 and D-4.

The two types of membranes were not tested simultaneously and therefore did not process composite waste with exactly the same characteristics. The collection of the samples for reuse took less than five hours in the case of the cellulose acetate membrane, and about ten hours for the dynamic membrane. In both instances, however, the concentrated residue had a high COD (3300 and 4850 mg/ℓ), was highly colored (Table D-3), and contained about 0.5% dissolved solids.

Since it may not always be desirable to attempt direct reuse or reclamation of the concentrate, the 90% recovery concentrate was used in the treatability tests.

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[a] Selas Corporation of America, Flotronics Division.

[b] Universal Oil Products, ROGA Division.

TABLE D-3. CHEMICAL ANALYSES OF WATER EVALUATED FOR REUSE[a] AT PLANT #70

(90% Water Recovery)

TYPE	UOP[b] Product	UOP Concentrate
SAMPLE NUMBER	611	613
DATE TAKEN	3/4/75	3/4/75
PARAMETER[c]		
COD	368	3300
BOD	80	260
TOC	84	750
Alkalinity	-50	-70
Hardness	<0.3	70
Total Solids	144	3620
Dissolved Solids	144	3608
Volatile Solids	80	1680
Color	10	450
Turbidity	0	50
Conductivity	135	2500
Phenol	0.05	0.08
pH	4.6	4.9
Mercury	0.002	0.003
Manganese	<0.01	0.56
Calcium	<0.01	2.25
Iron	0.57	1.37
Nickel	<0.1	0.21
Chromium	<0.01	0.21
Zinc	0.01	9.22
Copper	0.17	0.73
Magnesium	2.56	1.19

[a] Reuse tests conducted in Plant #70 dye laboratory.

[b] UOP module contained spiral-wound cellulose acetate membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE D-4. CHEMICAL ANALYSES OF WATER EVALUATED FOR REUSE[a] AT PLANT #70

(90% Water Recovery)

TYPE	Selas[b] Product	Selas Concentrate
SAMPLE NUMBER	607	609
DATE TAKEN	3/4/75	3/4/75
PARAMETER[c]		
COD	226	4850
BOD	56	840
TOC	88	480
Alkalinity	35	400
Hardness	≤0.3	45
Total Solids	272	5790
Dissolved Solids	272	5786
Volatile Solids	126	2050
Color	0	960
Turbidity	0	50
Conductivity	250	4500
Phenol	0.06	0.22
pH	8.5	7.4
Mercury	<0.001	<0.001
Manganese	<0.01	0.49
Calcium	0.01	3.16
Iron	0.79	1.06
Nickel	<0.1	0.49
Chromium	<0.01	<0.01
Zinc	0.08	0.56
Copper	0.1	0.21
Magnesium	1.72	1.09

[a] Reuse tests conducted in Plant #70 dye laboratory.

[b] Selas module contained ceramic tubes with dynamic membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

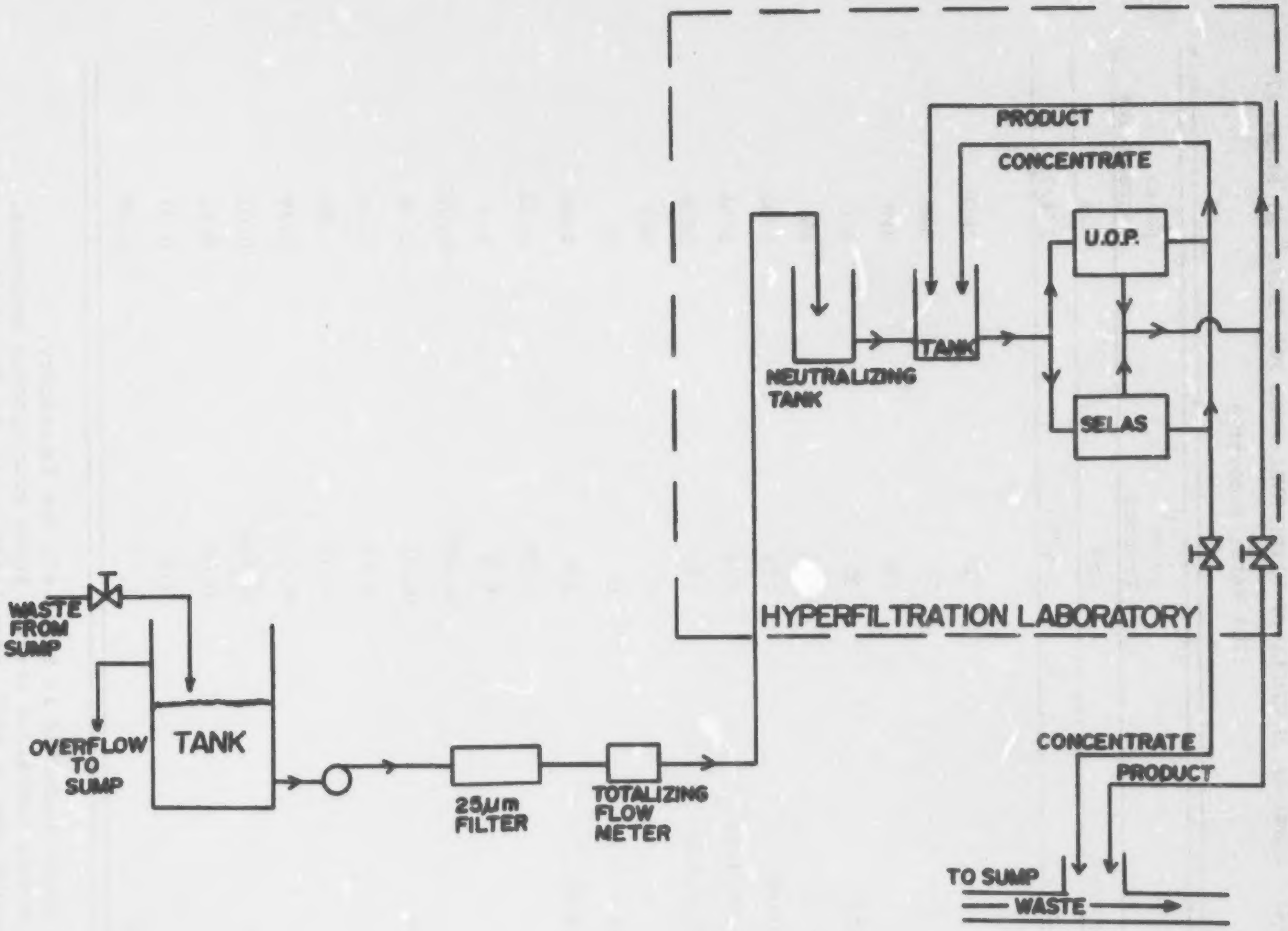
PRODUCT
CONCENTRATE
U.O.P.
TANK
NEUTRALIZING TANK
SELAS
HYPERFILTRATION LABORATORY
WASTE FROM SUMP
OVERFLOW TO SUMP
TANK
25μm FILTER
TOTALIZING FLOW METER
CONCENTRATE
PRODUCT
TO SUMP
WASTE

Figure D-1. Flow schematic for equipment set-up at Plant #70.

REUSE EVALUATION

Since most fibers processed by Plant #70 are acrylic (>98%), the waste stream contains mostly basic dyes. All these dyes, as well as the leveling agents and carriers used as auxilaries with them, can be recovered by hyperfiltration. Over 95% of the dyestuff is exhausted from the bath onto the fibers. Therefore, less than 5% of the dye is discharged to the waste stream. The auxiliary chemicals, which are not consumed in the process, are discharged with the wastewater and could be recovered. The analytical results for purified product and the concentrated residue, at the 90% recovery level by the cellulose acetate and dynamic membranes, are presented in Tables D-3 and D-4, respectively.

Reuse of Product Water

As a stringent test of the reuse of the product water, the 90% recovery samples were evaluated. The analyses of the product water (Table D-3) indicates that, in general, the COD and dissolved solids are more than expected for tap water, but the concentration of metals is less.

The product water was evaluated in the plant laboratory and found to be equivalent to normal process water. One of the two membrane units evaluated produced a slightly colored product water. The cause was traced to a mechanical breakdown rather than poor membrane rejection.

The specific procedure used by the Plant #70 dye laboratory for evaluation of the reuse of product water was as follows:

(1) Raise dyebath to 66°C (150°F).
(2) Add the following chemicals:

Sequesterene ST	0.10% of the weight of fabric
Sodium Acetate	1.00% of the weight of fabric
Chemogen RC-90	2.00% of the weight of fabric
Migrassist AC	2.00% of the weight of fabric
Glaubers Salt	5.00% of the weight of fabric
Basic Yellow 13	0.0095% of the weight of fabric
Basic Red 18	0.0410% of the weight of fabric
Basic Blue 3	0.0300% of the weight of fabric
Basic Blue 71	0.0970% of the weight of fabric

(3) Raise temperature at 1°/min to 43°C (110°F) and hold for 45 minutes.
(4) Cool.
(5) Rinse until clear.

Reuse of Concentrate

The attempts by the laboratory to use the concentrate in standard production procedures were not successful. The composite waste contained only small quantities of dye. No attempts were made to determine special formulations and to evaluate corresponding dye savings.

It is possible, when the wastewater and chemicals are recovered by hyperfiltration, to change the process to (1) achieve faster dyeing cycles, and/or (2) to eliminate the need for some auxiliary chemicals. For example, with direct dyeing of cellulose, salt can be eliminated by using higher concentrations of dye in the dyebath. Excess dyestuffs will be recovered by the membranes for reuse in the next cycle. Depending on the amount of fiber dyed and range of colors, this modification may or may not be practical. Water, chemicals, and energy requirements will play a major role in the selection of dyeing processes used in the future.

MEMBRANE PERFORMANCE

Both the cellulose acetate membrane and the dynamic membrane were operated on pretreated composite wastewater (Table D-5) for 200 hours beginning on March 7, 1975. The performance of the membranes was monitored by periodic measurements of the product water flow rate through the membranes and the conductivity rejection.

The wastewater feed to the UOP cellulose acetate and the dynamic Zr-PAA membranes was from a common tank. The incoming feed was neutralized and controlled at about pH ≃ 7 with sodium hydroxide. The volumetric recovery was allowed to rise to ∿80% by the withdrawal of product water and was maintained at 80% throughout the 200-hour test. The circulation velocities through the Selas module were changed at the 77-hour point in the test as shown in Figure D-2. The temperature was maintained at near 30°C because of temperature limitations of the cellulose acetate membrane.

Dynamic Membrane

Three different modules of Selas ceramic tubes with dynamic Zr-PAA membranes were evaluated. The performance is summarized in Figure D-2, a plot of flux and rejection throughout the test period. The characteristic initially rapid flux decline is evident. One of the modules, #9, was equipped with new membranes and therefore had a higher initial flux. Module #4 was equipped with ten-month old membranes that had already been used at several other plants. This older membrane exhibited a lower initial flux.

The effect of fluid velocity on the flux decline is illustrated in the figure. The operation of module #12 at 4.25 m/s (14 fps) may have permitted it to achieve a higher, more stable flux in the period from 77 to 200 hours. The lowering of the velocity in the other two modules at 77 hours caused a gradual decrease in flux.

The flux that would be used for design cost projections is 0.7 m/d (18 gallons/ft^2/d) at 28°C and 6.8 MPa (1000 psig), a value of only about 45% of the initial flux.

While the flux declined, the conductivity rejection increased. Both phenomena would be the result of the formation of a self-rejecting layer formed on the membrane surface from the constituents in the wastewater.

The conductivity rejection is a measure of the separation or filtration

TABLE D-5. CHEMICAL ANALYSES OF WASTEWATER TREATED[a] FOR MEMBRANE PERFORMANCE TESTS AT PLANT #70

SAMPLE NUMBER	618	623
DATE TAKEN	3/13/75	3/14/75
PARAMETER[b]		
COD	708	622
BOD	390	355
TOC	-	-
Alkalinity	43	41
Hardness	60	16
Total Solids	1216	1115
Dissolved Solids	1164	1065
Volatile Solids	-	-
Color	500	200
Turbidity	4.6	2.2
Conductivity	850	880
Phenol	0.012	0.008
pH	7.65	7.50
Mercury	-	-
Manganese	-	-
Calcium	0.400	0.320
Iron	0.025	0.050
Nickel	0.030	0.033
Chromium	0.020	0.020
Zinc	1.875	1.750
Copper	1.161	0.750
Magnesium	-	-

[a] Grab sample of combined effluent with 25-micron prefiltration, followed by neutralization to pH ∿ 7.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

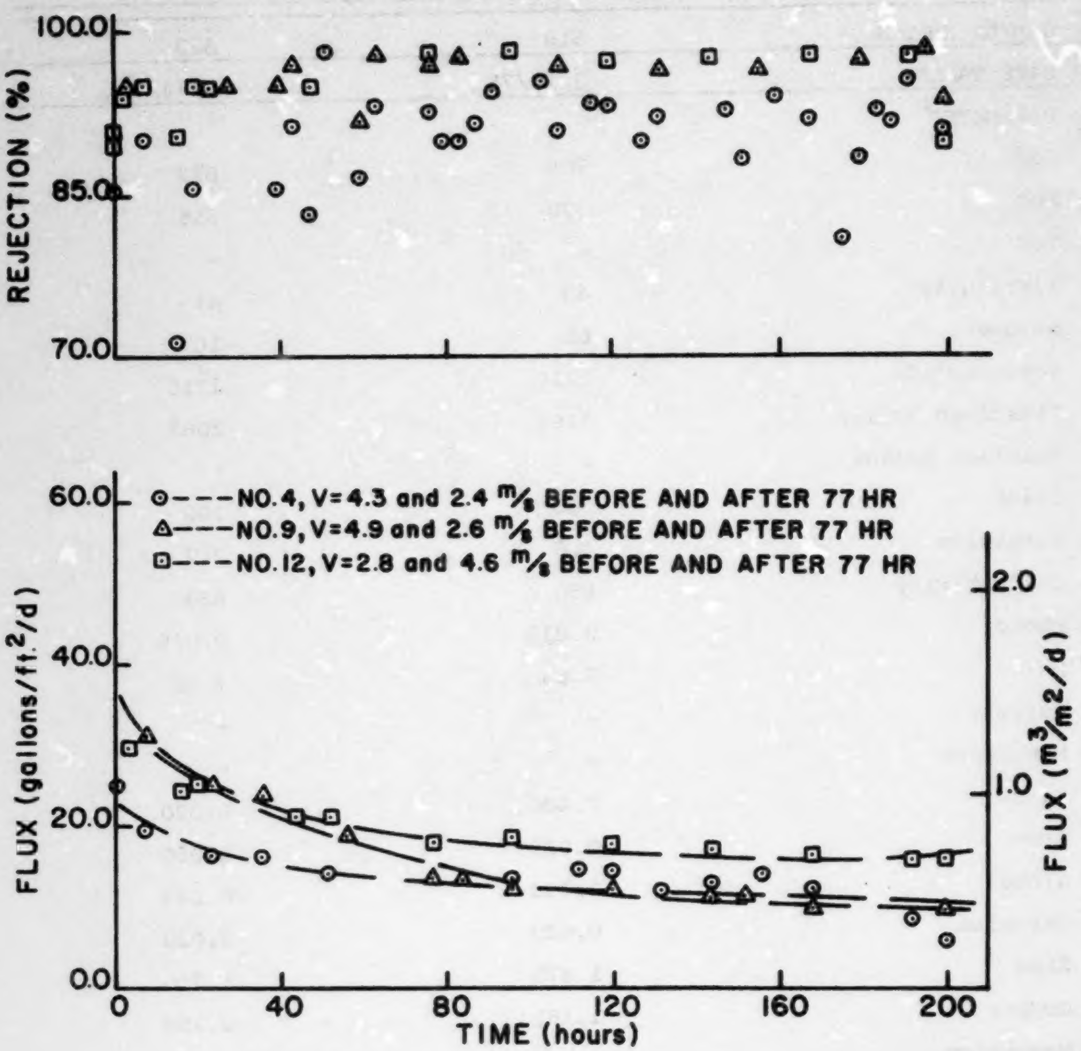

Figure D-2. Hyperfiltration of combined effluent at Plant #70 by Zr(IV)-PAA membranes on Selas ceramic supports. (P = 6.9 MPa (1000 psig); T = 28°C; pH = 5.5 - 7.6; recovery = 90%.)

of electrolytes by the membrane. The filtration efficiency for larger organic molecules is usually higher than for the electrolytes. Grab samples of the feed to the membrane and the product water passing through the membranes were obtained during the 200-hour performance tests and analyzed to indicate the filtration efficiency for several constituents. The results of analyses for three pairs of samples are shown in Tables D-6, D-7, and D-8.

The 95 - 99% rejections of organics, indicated by COD, BOD, and color comparisons between the concentrate and product samples are greater than the conductivity rejections. The phenol rejection is about 88%. The rejection of metals is very high, as indicated in cases where results are significantly above the limits of detection.

Cellulose Acetate Membrane

The performance of spiral-wound cellulose acetate membrane modules is illustrated in Figure D-3, a plot of the membrane flux and rejection throughout the test period. The operating conditions were as specified by the UOP module manufacturer: 2.76 MPa (400 psig), and a feed rate of 0.8 - 0.9 m^3/hr (3.5 - 4 GPM). This module had been used at two previous sites (Plant #50 and Plant #60).

The flux declined throughout the 200-hour test period during which time no washing procedures were attempted. The conductivity rejection was in the range of 90 - 95% throughout the test period. The rejection of other wastewater constituents was also very high, as indicated by the results of analyses of samples taken during the 200-hour test (see Tables D-9, D-10, and D-11).

TABLE D-6. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #70

SAMPLE NUMBER	614	615
TYPE	Concentrate	Product
DATE TAKEN	3/10/75	3/10/75
PARAMETER[b]		
COD	2661	94
BOD	2000	39
TOC	-	-
Alkalinity	38	9
Hardness	90	1
Total Solids	5600	183
Dissolved Solids	5480	177
Volatile Solids	-	-
Color	500	10
Turbidity	7.9	0.15
Conductivity	4100	190
Phenol	0.042	0.005
pH	7.15	7.60
Mercury	-	-
Manganese	-	-
Calcium	1.280	0.040
Iron	0.075	0.020
Nickel	0.567	0.030
Chromium	0.020	0.020
Zinc	3.125	0.005
Copper	2.464	0.018
Magnesium	-	-

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

TABLE D-7. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #70

SAMPLE NUMBER	622	621
TYPE	Product	Concentrate
DATE TAKEN	3/13/75	3/13/75
PARAMETER[b]		
COD	51	2303
BOD	45	2200
TOC	-	-
Alkalinity	8	83
Hardness	2	110
Total Solids	159	5448
Dissolved Solids	159	5412
Volatile Solids	-	-
Color	5	500
Turbidity	0.10	4.1
Conductivity	170	4400
Phenol	0.005	0.661
pH	7.40	7.55
Mercury	-	-
Manganese	-	-
Calcium	0.040	0.330
Iron	0.020	0.025
Nickel	0.030	0.500
Chromium	0.020	0.020
Zinc	0.005	3.042
Copper	0.018	2.946
Magnesium	-	-

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

TABLE D-8. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #70

SAMPLE NUMBER	624	625
TYPE	Concentrate	Product
DATE TAKEN	3/14/75	3/14/75
PARAMETER[b]		
COD	2280	51
BOD	1450	48
TOC	-	-
Alkalinity	72	11
Hardness	90	1
Total Solids	5585	233
Dissolved Solids	5535	227
Volatile Solids	-	-
Color	500	5
Turbidity	1.9	0.20
Conductivity	3700	190
Phenol	0.055	0.005
pH	8.00	7.25
Mercury	-	-
Manganese	-	-
Calcium	0.800	0.040
Iron	0.020	0.020
Nickel	0.030	0.030
Chromium	0.020	0.020
Zinc	0.005	0.005
Copper	0.010	0.018
Magnesium	-	-

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

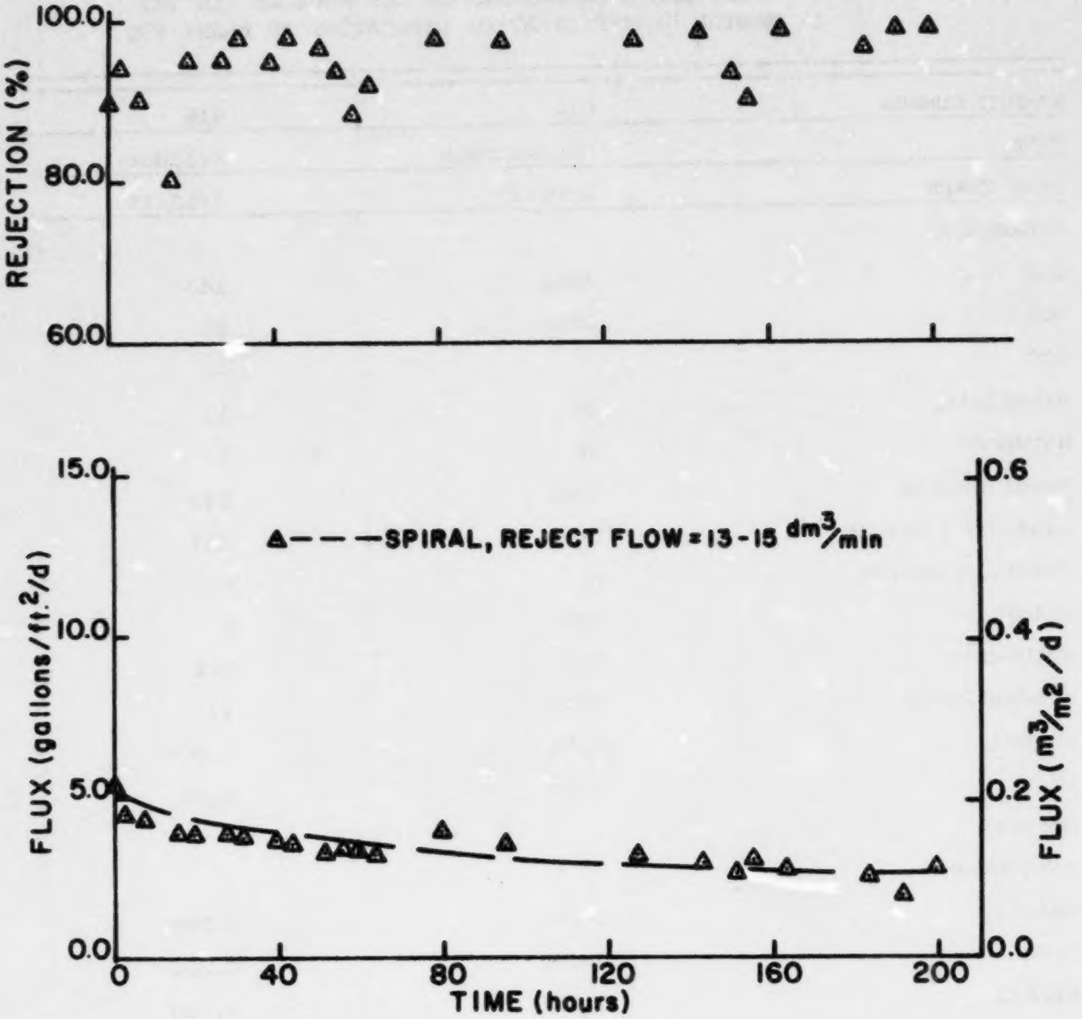

Figure D-3. Hyperfiltration of combined effluent at Plant #70 by a UOP spiral-wound module with cellulose acetate membranes. (P = 2.8 MPa (400 psig); T = 26°C; pH = 4.1 - 7.7; recovery = 90%.)

TABLE D-9. PERFORMANCE PARAMETERS OF UOP MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #70

SAMPLE NUMBER	614	616
TYPE	Concentrate	Product
DATE TAKEN	3/10/75	3/10/75
PARAMETER[b]		
COD	2661	140
BOD	2000	80
TOC	-	-
Alkalinity	38	11
Hardness	90	1
Total Solids	5600	143
Dissolved Solids	5480	137
Volatile Solids	-	-
Color	500	5
Turbidity	7.9	2.1
Conductivity	4100	52
Phenol	0.042	0.005
pH	7.15	6.70
Mercury	-	-
Manganese	-	-
Calcium	1.280	0.080
Iron	0.075	0.020
Nickel	0.567	0.030
Chromium	0.020	0.020
Zinc	3.125	0.005
Copper	2.464	0.010
Magnesium	-	-

[a] UOP module contained spiral-wound cellulose acetate membranes.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

TABLE D-10. PERFORMANCE PARAMETERS OF UOP MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #70

SAMPLE NUMBER	621	620
TYPE	Concentrate	Product
DATE TAKEN	3/13/75	3/13/75
PARAMETER[b]		
COD	2303	148
BOD	2200	36
TOC	-	-
Alkalinity	83	9
Hardness	110	1
Total Solids	5448	76
Dissolved Solids	5412	64
Volatile Solids	-	-
Color	500	5
Turbidity	4.1	0.35
Conductivity	4400	66
Phenol	0.661	0.005
pH	7.55	6.85
Mercury	-	-
Manganese	-	-
Calcium	0.330	0.040
Iron	0.025	0.020
Nickel	0.500	0.030
Chromium	0.020	0.020
Zinc	3.042	0.005
Copper	2.946	0.010
Magnesium	-	-

[a] UOP module contained spiral-wound cellulose acetate membranes.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

TABLE D-11. PERFORMANCE PARAMETERS OF UOP MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #70

SAMPLE NUMBER	624	626
TYPE	Concentrate	Product
DATE TAKEN	3/14/75	3/14/75
PARAMETER[b]		
COD	2280	156
BOD	1450	32
TOC	-	-
Alkalinity	72	10
Hardness	90	1
Total Solids	5585	83
Dissolved Solids	5535	77
Volatile Solids	-	-
Color	500	5
Turbidity	1.9	0.45
Conductivity	3700	120
Phenol	0.055	0.005
pH	8.00	7.30
Mercury	-	-
Manganese	-	-
Calcium	0.800	0.040
Iron	0.020	0.020
Nickel	0.030	0.033
Chromium	0.020	0.020
Zinc	0.005	0.005
Copper	0.010	0.005
Magnesium	-	-

[a] UOP module contained spiral-wound cellulose acetate membranes.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (NTU), conductivity (μmho/cm), and pH (unitless).

APPENDIX E

PLANT #40

The on-site tests conducted from March 26, 1975, to April 23, 1975, were to obtain the following information: (1) plant laboratory evaluation of reuse, and (2) engineering performance data with membranes. Reuse of both the purified product water and the concentrated residue was evaluated in laboratory tests conducted by Plant #40 personnel. Samples of wastewater, purified product water, and concentrated residue were analyzed by Nardin Laboratory.[a] In addition, the treatability of the concentrated residue was evaluated in bench-scale tests, Appendix J.

The production parameters of Plant #40, Table E-1, provide a basis for evaluation of the results of the project. The factors are important in the evaluation of the practicality of scale-up from the pilot plant.

FIBERS AND CHEMICALS

Plant #40 is presently operated to scour, bleach, dye, and finish cotton and cotton/polyester blended fabrics on continuous ranges. The chemicals and dyes used by the plant are those which are common to the finishing of cotton and polyester fibers: sulfur, vat, fiber reactive, disperse, and napthol dyes.

Ninety percent of the 20,833 m^3/d (5,500,000 gallons/day) total water usage is in the plant. Allowing for evaporation in drying, the composite waste stream is at least 85% by volume plant wastewater.

WASTEWATER CHARACTERISTICS

The variety of dyes and scouring chemicals used produce a complex and variable waste stream composition. The wastewater characteristics, based on a monthly average for the summer of 1974, of plant wastewater discharge parameters are: BOD_5 = 350 mg/ℓ; COD 1290 mg/ℓ; total suspended solids = 346 mg/ℓ; total dissolved solids = 3310 mg/ℓ; pH = 11.6; temperature = 100°F. Tables E-2, E-3, and E-4 present the results of analyses for eight grab

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[a] Division of Commonwealth Laboratory, Inc., Greenville, SC.

TABLE E-1. PLANT #40 PRODUCTION CAPACITY PARAMETERS

QUANTITIES USED	
Materials: cotton, cotton/polyester	
Water (total to plant), m^3/day	20,833
(gallons/day)	(5,500,000)
Water (wet finishing), m^3/day	20,545
(gallons/day)	(5,400,000)
Dyes, kg/day	8,353
(pounds/day)	(18,565)
Auxiliary Chemicals, kg/day	39,342
(pounds/day)	(86,750)
Energy (for process steam), joules/day	7358×10^9
(Btu/day)	(7008×10^6)
UNIT COSTS	
Water, ¢/m^3	2
($/1000 gallons)	(0.06)
Fuel, ¢/10^7 joules	2.0
($/$10^6$ Btu)	(2.20)

TABLE E-2. CHEMICAL ANALYSES OF PLANT #40 WASTEWATER[a]

SAMPLE NUMBER	633	648	654
DATE TAKEN	4/2/75	4/3/75	4/7/75
PARAMETER[b]			
COD	1360	1520	1860
BOD	270	330	380
TOC	534	620	563
Alkalinity	1549	1424	1158
Hardness	13	15	13
Total Solids	4000	3140	3812
Dissolved Solids	2920	2888	3634
Volatile Solids	768	910	1020
Color	350	250	300
Turbidity	6.0	10	5.5
Conductivity	6400	5800	4500
Phenol	0.004	0.097	0.053
pH	11.7	11.7	11.5
Mercury	<0.1	<0.1	<0.1
Manganese	<0.04	<0.04	<0.04
Calcium	2.0	2.5	1.5
Iron	0.2	0.2	0.2
Nickel	0.1	0.1	0.1
Chromium	13	0.15	31
Zinc	2.2	1.3	3.2
Copper	0.4	0.2	0.4
Magnesium	1.9	2.0	1.8

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (mg/ℓ SIO_2), conductivity (μmho/cm), pH (unitless), and mercury (μg/ℓ).

TABLE E-3. CHEMICAL ANALYSES OF PLANT #40 WASTEWATER[a]

SAMPLE NUMBER	655	661	667
DATE TAKEN	4/7/75	4/8/75	4/9/75
PARAMETER[b]			
COD	1340	1420	1460
BOD	360	340	420
TOC	615	558	547
Alkalinity	1408	1483	1599
Hardness	14	38	12
Total Solids	2784	2990	3344
Dissolved Solids	2568	2840	3226
Volatile Solids	576	620	912
Color	200	250	150
Turbidity	6.5	13	14
Conductivity	6700	6500	7100
Phenol	0.097	0.159	0.060
pH	11.8	11.8	11.8
Mercury	<0.1	<0.1	<0.1
Manganese	0.04	0.04	0.04
Calcium	1.2	2.2	1.8
Iron	0.2	0.2	0.2
Nickel	0.1	0.1	0.1
Chromium	61	8	13
Zinc	4.3	5.6	1.1
Copper	1.6	1.0	1.0
Magnesium	2.1	10.8	1.7

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (mg/ℓ SIO_2), conductivity (μmho/cm), pH (unitless), and mercury (μg/ℓ).

TABLE E-4. CHEMICAL ANALYSES OF PLANT #40 WASTEWATER[a]

SAMPLE NUMBER	668	677
DATE TAKEN	4/9/75	4/10/75
PARAMETER[b]		
COD	1424	1160
BOD	585	350
TOC	372	666
Alkalinity	1650	1674
Hardness	10	14
Total Solids	3750	3388
Dissolved Solids	3670	3190
Volatile Solids	1900	1082
Color	720	100
Turbidity	170	7.0
Conductivity	8200	6500
Phenol	0.10	0.080
pH	11.9	11.8
Mercury	1.0	<0.1
Manganese	<0.01	0.08
Calcium	0.96	1.5
Iron	2.25	2
Nickel	0.47	0.1
Chromium	5.13	3
Zinc	2.20	1.5
Copper	1.52	9.0
Magnesium	2.06	2.2

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (mg/ℓ SIO_2), conductivity (μmho/cm), pH (unitless), and mercury (μg/ℓ).

samples obtained during the period of on-site testing. Plant #40 is classified as Subcategory 4, woven fabric dyeing and finishing.[a]

SCHEDULE AND PROCEDURE

Schedule

Testing was begun on April 1, 1975. Initially, one-gallon (3.8ℓ) samples of purified product and concentrate were collected for reuse evaluation in the plant laboratory. The UOP module was then taken out of operation for the remainder of Plant #40's testing program. A 38ℓ sample of concentrate was later collected for the biological treatability study.

The following is a summary of events at Plant #40:

03/26 - Arrived from Plant #70; utilities connected.

04/01 - Began parametric performance test with Westinghouse polysulfone ultrafilter and Selas modules.

04/02 - Reuse test samples generated.

04/11 - Parametric performance test completed.

04/15 - Began special tests.

04/22 - Special tests completed.

04/23 - Departed to Plant #80.

Procedure

The membranes for evaluation were selected based on availability and the characteristics of the wastewater. The wastewater was prefiltered through 25-micron cartridge filters prior to entering the mobile laboratory. The pH was adjusted when necessary to meet membrane manufacturer specifications. Figure E-1 shows schematically the equipment arrangement. Three types of membranes were employed in these tests: the UOP[b] spiral-wound cellulose acetate membrane, the dual-layer dynamic membrane on the Selas[c] ceramic tubes, and the Westinghouse[d] tubular polysulfone ultrafilter.

REUSE

All types of membranes were used to generate samples for reuse

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[a] Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Textile Point Source Category. EPA-440/1-74-022-a, US Environmental Protection Agency, Washington, DC, 1974.

[b] Universal Oil Products, ROGA Division.

[c] Selas Corporation of America, Flotronics Division.

[d] Westinghouse Membrane Systems was sold to Union Carbide.

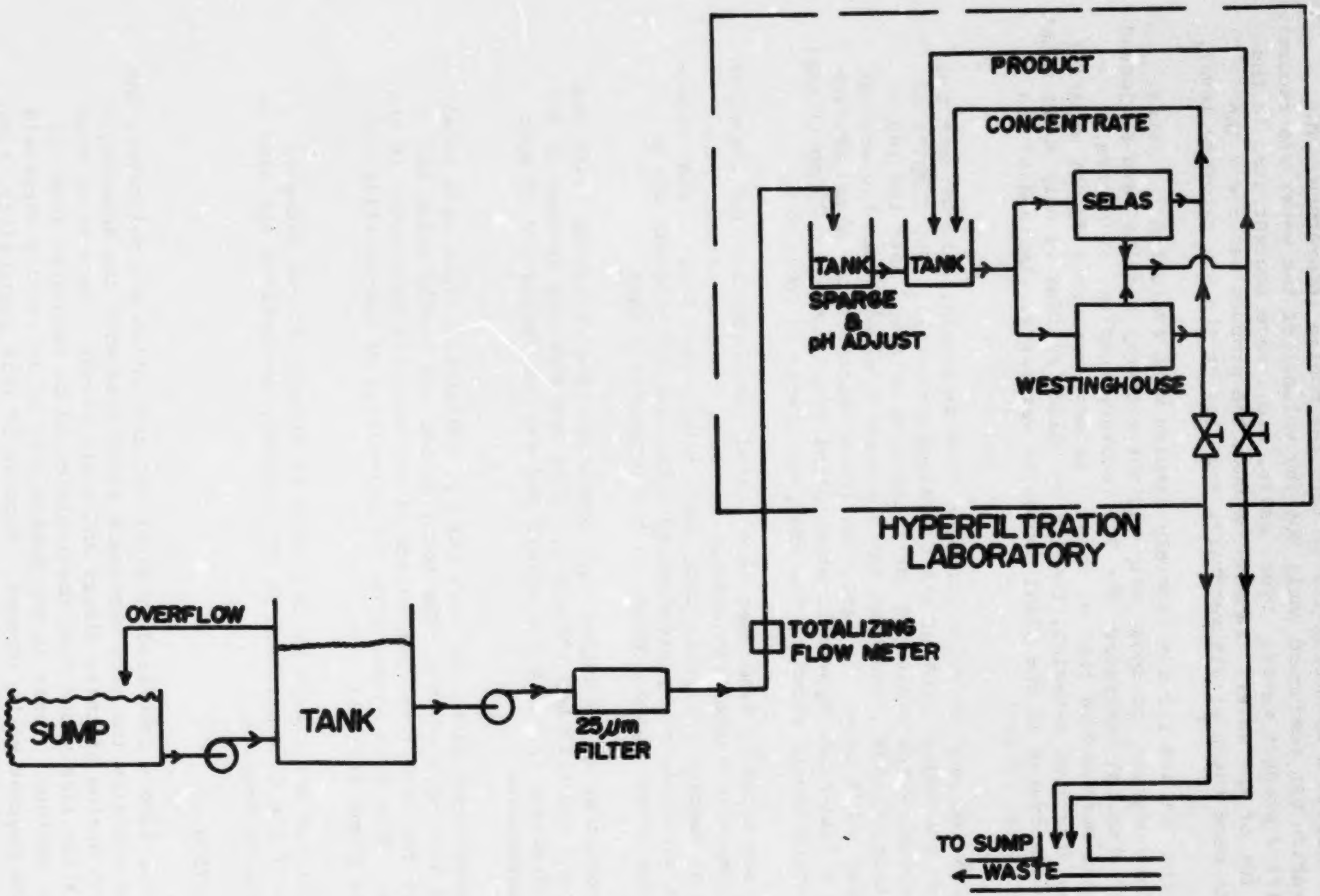
PRODUCT
CONCENTRATE
SELAS
TANK
TANK
SPARGE & pH ADJUST
WESTINGHOUSE
HYPERFILTRATION LABORATORY
OVERFLOW
SUMP
TANK
TOTALIZING FLOW METER
25 µm FILTER
TO SUMP
WASTE

Figure E-1. Flow schematic for equipment set-up at Plant #40.

evaluation. A sample of composite wastewater was drawn from the plant sewer, and pumped through a 25-micron filter into the mobile laboratory. The hyperfiltration was conducted until 90% (by volume) of the water was recovered as purified product water. Dyes, salts, etc., were concentrated in the remaining 10% of the water. Samples of both the product water and the concentrate were taken at 75% recovery, and also at the 90% recovery level.

Both the 75% and the 90% recovery samples were evaluated for reuse. However, for budgetary reasons, only the 90% recovery samples were subjected to detailed chemical analyses. The 90% recovery samples, of course, represent the more severe test of reuse. Because membranes do not separate 100% of the dissolved material, the 10% by volume residue is only about eight times as concentrated as the plant composite wastewater (instead of the volumetric factor of ten).

The purified product water contains some chemicals, also because the membranes do not reject 100% of the dissolved materials. The samples of purified product water evaluated for reuse were obtained near the end of the concentration (90%), and thus contain more chemicals than the average product water would have. In fact, for these membranes the mixed product water from a full-scale hyperfiltration plant would contain only about one-third the contaminants shown by the analyses listed in Table E-5.

The three types of membranes were tested simultaneously and therefore processed composite waste with exactly the same characteristics. The collection of samples for reuse took about twenty-four hours. The concentration was accomplished by withdrawing Selas and UOP products while recycling the Westinghouse product to the concentrate tank.

The product water contained high concentrations of solids (1440 and 1222 mg/ℓ) and COD (218 and 178 mg/ℓ). This was expected because of the high concentrations in the waste stream and was not indicative of poor membrane performance.

The concentrate water was very strong, containing 12210 mg/ℓ total solids, and 5020 mg/ℓ of COD. The total solids are mostly salts as indicated by the high (78%) percentage of non-volatile substances in the concentrate. This data agrees with the percentage of non-volatile salt found in the plant effluent (77%).

Since it may not always be desirable to attempt direct reuse or reclamation of the concentrate, the 90% recovery concentrate was used in the treatability tests.

REUSE EVALUATION

Since the fibers processed by Plant #40 are cotton and polyester, the waste stream contains the many chemicals associated with the scouring, desizing, and dyeing of these fibers and their blends. Because of this there was little likelyhood that chemicals could be recovered from the concentrated residue. There is the possibility of recovering chemicals from isolated process waste streams. Because of this possibility, rinse

TABLE E-5. CHEMICAL ANALYSES OF WATER EVALUATED FOR REUSE[a] AT PLANT #40
(90% Water Recovery)

TYPE	Selas[b] Product	UOP[c] Product	West[d] Product	S/UOP/W Concentrate
SAMPLE NUMBER	643	644	645	646
DATE TAKEN	4/2/75	4/2/75	4/2/75	4/2/75
PARAMETER[e]				
COD	218	178	1780	5020
BOD	58	40	795	1800
TOC	27.5	25.5	480	1200
Alkalinity	73	32	290	270
Hardness	3	<1	70	105
Total Solids	1440	1222	9356	12210
Dissolved Solids	1432	1222	9337	12120
Volatile Solids	140	122	830	2698
Color	20	30	300	2500
Turbidity	10	20	60	400
Conductivity	2200	1650	12000	13600
Phenol	0.01	0.22	0.16	0.21
pH	7.0	6.4	7.1	6.4
Mercury	<0.001	<0.001	<0.001	<0.001
Manganese	0.27	<0.1	<0.1	0.25
Calcium	0.36	<0.01	<0.01	0.74
Iron	1.76	1.79	0.87	3.80
Nickel	<0.1	<0.1	0.26	0.1
Chromium	<0.1	<0.1	0.64	3.60
Zinc	0.30	0.133	2.88	9.30
Copper	0.112	<0.1	1.16	5.51
Magnesium	1.97	1.77	1.07	2.17

[a] Reuse tests conducted in Plant #40 dye laboratory.
[b] Selas module contained ceramic tubes with dynamic membranes.
[c] UOP module contained spiral-wound cellulose acetate membranes.
[d] Westinghouse module contained tubular polysulfone ultrafilter membranes.
[e] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

water from the indigo range was subjected to hyperfiltration concentration. The analyses results for the purified product water and the concentrated residue from both the cellulose acetate and the dynamic membranes are presented in Table E-5.

Reuse of Product Water

As a stringent test of the reuse of the product water, the 90% recovery samples were evaluated. The analyses of the product water indicates that, in general, the COD and dissolved solids are much more than expected for tap water.

All of the purified product water generated by the mobile laboratory at Plant #40 was evaluated in the plant laboratory and found suitable for reuse in the plant.

The product water was used in the laboratory to dye a bottle green reactive dye formulation on a 100% cotton sateen fabric. It was also used in a padding formulation containing no dye to determine if any background color would interfere with continuous pad-dry-thermosol-steam operation.

Laboratory pad evaluation was conducted to identify color impurities in the product water which would interfere with continuous dyeing. No stains or colorations were detected which would interfere with continuous dyeing.

The product water was padded onto the trial fabric as would normally be run in laboratory dyeings. No additives or dyestuffs were added to the sample water. The fabrics used were Super Twill (100% cotton), and Equestrian Twill (65% polyester/35% cotton).

Both fabrics were run simultaneously with regular plant water used as the control. For the 100% cotton fabric, fabric samples were retained after the pad-drying process and again after the final treatment which is steaming, rinsing, oxidizing, and drying. For the polyester/cotton fabric, fabric samples were retained after the pad-drying process, again after thermosoling, and after the final treatment, which is steaming, rinsing, oxidizing, and drying. These fabric samples are available for further testing and evaluation.

The procedures employed in the test dyeing of Super Twill, 100% cotton, were standard for continuous running.

For the trial fabric Equestrian Twill, 65% polyester/35% cotton, all procedures were the same as those for the Super Twill fabric with the exception that after drying through the Fosteria unit the fabric was thermosoled for ninety seconds at 410°F.

No problems were encountered with the use of the product water for laboratory test dyeings and the fastness properties of the dyed fabric were the same as those obtained with normal plant water.

Reuse of Concentrate

The concentrates resulting from 70% and 95% recoveries were evaluated in the laboratory for a pad-dry-thermosol-steam procedure. Minimal dye concentration was obtained on the treated fabric giving evidence of small concentrations of a mixture of dyes and chemicals in the concentrate. No value could be observed from reuse of the concentrate obtained from the composite waste stream.

A sample of indigo rinse water was concentrated by the hyperfiltration membranes to evaluate the recovery of indigo dye. The concentrate obtained was then evaluated by plant laboratory personnel. The results indicated that the concentrated indigo rinse water could be used to formulate a dyeing solution for reuse with equivalent fastness properties to the original dye. A significant savings of indigo was indicated by the laboratory results.

It is possible, when the wastewater and chemicals are recovered by hyperfiltration, to change the process to (1) achieve faster dyeing cycles, and/or (2) to eliminate the need for some auxiliary chemicals. For example, with direct dyeing of cellulose, salt can be eliminated by using higher concentrations of dye in the dyebath. Excess dyestuffs will be recovered by the membranes for reuse in the next cycle. Depending on the amount of fiber dyed and range of colors, this modification may or may not be practical. Water, chemicals, and energy requirements will play a major role in the selection of dyeing processes used in the future.

MEMBRANE PERFORMANCE

The polysulfone ultrafilter and the dynamic membrane were operated on pretreated composite wastewater (Table E-2) for 200 hours beginning on April 1, 1975. The performance of the membranes was monitored by periodic measurements of the product water flow rate through the membranes and the conductivity rejection.

The Westinghouse polysulfone and the dynamic Zr-PAA membranes were fed from a common tank. The incoming feed was neutralized to pH ≈ 7 - 9.5 with sulfuric acid and controlled in that range. Tables E-6 and E-7 show analyses performed on feed water after neutralization and 25-micron filtration. The volumetric recovery was allowed to rise to ~90%, to obtain samples for reuse evaluation, but was then lowered to 80% and maintained there throughout the remainder of the 200-hour test. The temperature was maintained at near 45°C, the average temperature of the plant outfall. At about midway in the test a cooling water stoppage occurred causing excessive loop temperature and the rupture of modules #4 and #12. Module #9, a previously used module, was substituted for #12, the position of #4 was plugged, and the test continued.

Dynamic Membrane

Four modules of Selas ceramic tubes with dynamic Zr-PAA membranes were evaluated. The performance is summarized in Figure E-2, a plot of flux and rejection throughout the test period. One of the modules, #11, was equipped

TABLE E-6. CHEMICAL ANALYSES OF WASTEWATER TREATED[a] FOR MEMBRANE PERFORMANCE TESTS AT PLANT #40

SAMPLE NUMBER	649	656	662
DATE TAKEN	4/3/75	4/7/75	4/8/75
PARAMETER[b]			
COD	1300	1280	1280
BOD	250	280	310
TOC	399	408	499
Alkalinity	0	83	124
Hardness	12	17	25
Total Solids	3516	4832	5038
Dissolved Solids	3362	3432	4864
Volatile Solids	598	618	76
Color	50	100	100
Turbidity	9.5	5.5	3.0
Conductivity	3600	3700	3400
Phenol	0.077	0.153	0.045
pH	6.3	6.8	6.0
Mercury	<0.1	-	-
Manganese	0.04	0.12	0.08
Calcium	0.6	0.87	0.80
Iron	1.0	0.2	3
Nickel	0.1	0.1	0.1
Chromium	2.5	5	3
Zinc	2	3.5	4.0
Copper	0.5	1.4	1.6
Magnesium	1.5	3.0	6.6

---

[a] Grab samples of combined effluent with 25-micron prefiltration, followed by neutralization to pH $\sim$ 6.5.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (mg/ℓ SIO_2), conductivity (µmho/cm), pH (unitless), and mercury (µg/ℓ).

TABLE E-7. CHEMICAL ANALYSES OF WASTEWATER TREATED[a] FOR MEMBRANE PERFORMANCE TESTS AT PLANT #40

SAMPLE NUMBER	669	678
DATE TAKEN	4/9/75	4/10/75
PARAMETER[b]		
COD	1600	1080
BOD	400	300
TOC	723	361
Alkalinity	174	1424
Hardness	27	11
Total Solids	6030	4516
Dissolved Solids	5726	3076
Volatile Solids	958	528
Color	350	100
Turbidity	7.0	0
Conductivity	5800	3200
Phenol	0.103	0.020
pH	6.3	5.9
Mercury	-	-
Manganese	0.2	0.08
Calcium	1.4	0.93
Iron	2.8	1
Nickel	0.3	0.1
Chromium	13	8
Zinc	3.7	1.7
Copper	2.2	1.3
Magnesium	4.8	1.6

[a] Grab samples of combined plant effluent with 25-micron prefiltration, followed by neutralization to pH ∿ 6.0.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (mg/ℓ SIO_2), conductivity (μmho/cm), and pH (unitless).

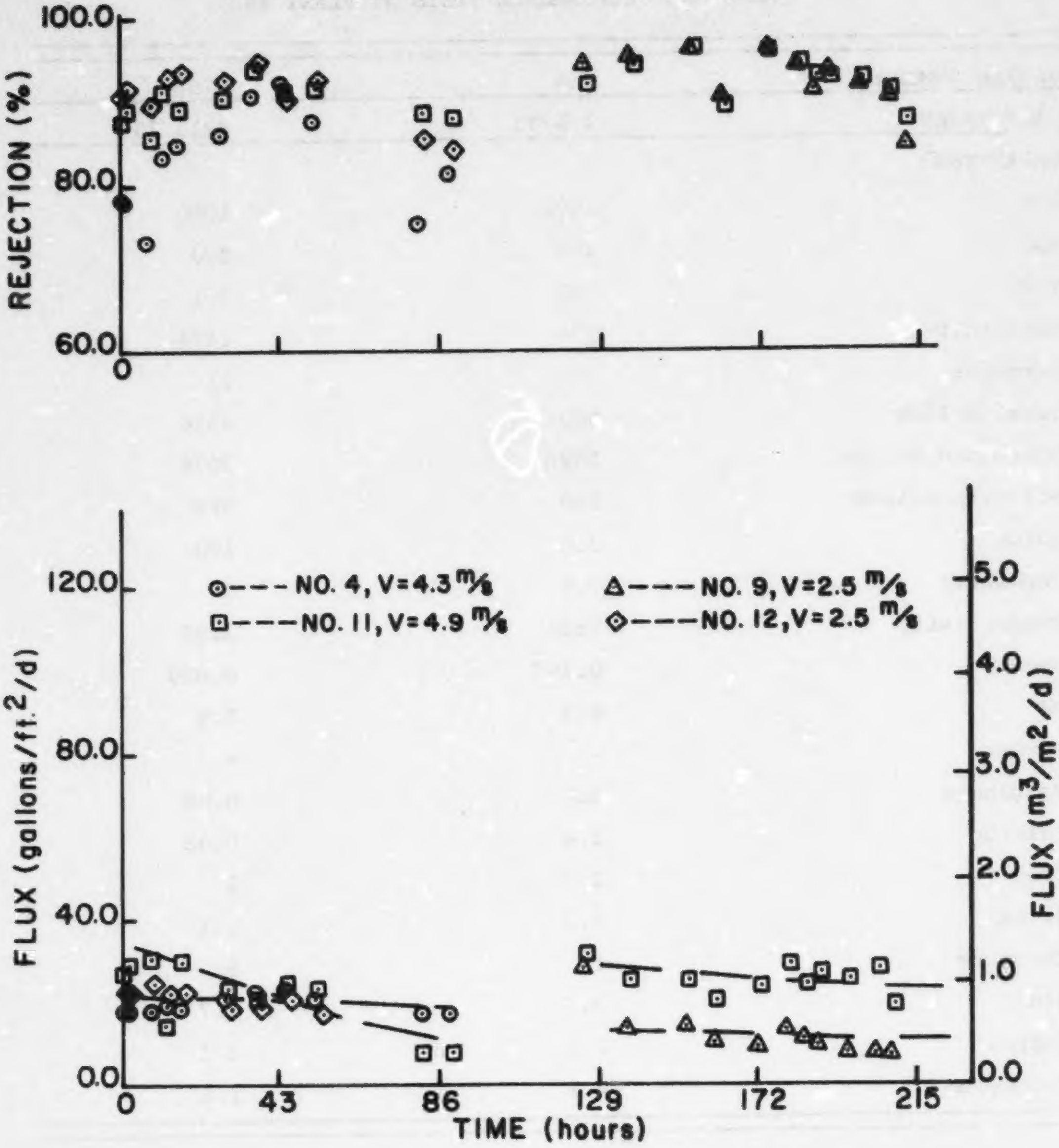

Figure E-2. Hyperfiltration of combined effluent at Plant #40 by Zr(IV)-PAA membranes on Selas ceramic supports. (P = 6.9 MPa (1000 psig); T = 45°C; pH = 7.0 - 9.5; recovery = 75%.)

with new membranes and therefore had a somewhat higher initial flux. Module #4 was equipped with ten-month old membranes that had already been used at several other plants. This older membrane exhibited a lower initial flux. Table E-8 shows the analyses of product water from module #4, and the corresponding concentrate.

The effect of fluid velocity on flux decline was the subject of parametric testing. But the rupture of modules #4 and #12 near the midpoint of the tests prevented an adequate comparison between low velocity (2.5 m/s) and high velocity (4.9 m/s) flux decline rates. Module #11 operating at 4.9 m/s did achieve a stable flux of 1.0 m/d (25 gallons/ft^2/d) at 45°C and 6.9 MPa (1000 psig). This flux is used in design cost projections.

The somewhat erratic conductivity rejections are the result of the widely varying pH (7 - 9.5) throughout the test.

The conductivity rejection allows measurement of the electrolyte filtration by the membrane. The filtration efficiency for larger organic molecules is usually higher than for the electrolytes. Grab samples of the concentrate and product waters passing through the membranes were obtained during the 200-hour performance tests and analyzed to indicate the filtration efficiency for several constituents. The results of analyses for three pairs of samples are shown in Tables E-8 through E-13.

The high rejections of organics, indicated by COD, BOD, and color comparisons between the concentrate and product samples are greater than the conductivity rejections. The phenol rejection is about 88%. The rejection of metals is very high, as indicated in cases where results are significantly above the limit of detection.

Indigo dye waste was selected as the feed of interest for the special tests. Figure E-3 shows data taken during two runs. During the first 50 hours a composite wash water from the total dye range was processed to 90% volumetric recovery. The waste was processed as received at a pH of 8.5. The loop was then drained and indigo waste taken from the first hot rinse box on the range was introduced without pH adjustment at a pH of 11.2. A cluster of porous ceramic tubes normally used on a membrane support was installed in the loop.

Polysulfone Ultrafilter

The performance of the tubular polysulfone ultrafiltration module is summarized in Figure E-4, a plot of the flux and rejection throughout the test period. The operating conditions were as specified by the manufacturer: 2.1 MPa (300 psig), a feed rate of 8.3 - 13.6 dm^3/min (2.3 - 3.6 GPM), and a temperature of 40°C. This module was first used at this site.

The flux showed a rapid decline to 0.1 m/d (2.5 gallons/ft^2/d) while the rejection rose to near 60%, presumably due to the formation of a self-rejecting fouling layer formed from feed constituents. No washing procedures were attempted.

TABLE E-8. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #40

SAMPLE NUMBER	650[b]	651[c]	653
TYPE	Product	Product	Concentrate
DATE TAKEN	4/3/75	4/3/75	4/3/75
PARAMETER[d]			
COD	142	80	1100
BOD	20	120	580
TOC	223	30	1256
Alkalinity	74	49	33
Hardness	0.10	0.22	43
Total Solids	464	698	9250
Dissolved Solids	460	698	8854
Volatile Solids	52	68	2142
Color	0	0	200
Turbidity	5.0	8	13.0
Conductivity	890	1200	8300
Phenol	0.02	0.0415	0.065
pH	7.4	7.0	5.9
Mercury	-	-	0.043
Manganese	0.04	0.04	0.08
Calcium	0.74	0.06	1.7
Iron	-	-	8
Nickel	-	0.1	0.7
Chromium	0.15	0.15	15
Zinc	0.07	0.1	5.8
Copper	0.04	0.08	3.3
Magnesium	0.08	0.08	9.2

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] Combined product from modules #4, #11, and #12.

[c] Product from module #4.

[d] All results are in mg/ℓ, except for color (APHA units), turbidity (mg/ℓ SIO_2), conductivity (μmho/cm), pH (unitless), and mercury (μg/ℓ).

TABLE E-9. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #40

SAMPLE NUMBER	657	660
TYPE	Product	Concentrate
DATE TAKEN	4/7/75	4/7/75
PARAMETER[b]		
COD	320	1650
BOD	95	360
TOC	26	1392
Alkalinity	0	266
Hardness	0.7	52
Total Solids	500	11976
Dissolved Solids	488	11566
Volatile Solids	90	2180
Color	5	800
Turbidity	11	11
Conductivity	690	10000
Phenol	0.030	0.161
pH	6.8	6.3
Mercury	-	<0.057
Manganese	0.04	0.4
Calcium	0.07	2.3
Iron	-	10.6
Nickel	-	1.7
Chromium	0.15	13
Zinc	0.05	5.8
Copper	0.04	2.4
Magnesium	0.02	11.4

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (mg/ℓ SIO_2), conductivity (μmho/cm), pH (unitless), and mercury (μg/ℓ).

TABLE E-10. PERFORMANCE PARAMETERS OF SELAS AND WESTINGHOUSE MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #40

TYPE	Selas[a] Product	Westinghouse[b] Product	Selas/West Concentrate
SAMPLE NUMBER	663	665	666
DATE TAKEN	4/8/75	4/8/75	4/8/75
PARAMETER[c]			
COD	180	1500	1400
BOD	80	350	680
TOC	23	548	1271
Alkalinity	66	124	349
Hardness	0.73	21	51
Total Solids	356	6266	1400
Dissolved Solids	356	6084	10062
Volatile Solids	72	932	2278
Color	20	150	400
Turbidity	4	5.5	7.0
Conductivity	470	6400	9700
Phenol	0.040	0.1435	0.109
pH	6.4	6.6	6.2
Mercury	-	-	<0.057
Manganese	0.04	0.12	0.4
Calcium	0.07	-	2.4
Iron	-	-	14
Nickel	0.1	-	1.9
Chromium	0.15	-	13
Zinc	0.05	0.2	5.8
Copper	0.1	-	3.2
Magnesium	0.04	-	12.4

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] Westinghouse module contained tubular polysulfone ultrafilter membranes.

[c] All results are in mg/ℓ, except for color (APHA units), turbidity (mg/ℓ SIO_2), conductivity (μmho/cm), pH (unitless), and mercury (μg/ℓ).

TABLE E-11. PERFORMANCE PARAMETERS OF SELAS AND WESTINGHOUSE MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #40

TYPE	Selas[a] Product	Westinghouse[b] Product	Selas/West Concentrate
SAMPLE NUMBER	670	672	673
DATE TAKEN	4/9/75	4/9/75	4/9/75
PARAMETER[c]			
COD	200	1160	1400
BOD	30	170	590
TOC	20	489	960
Alkalinity	99	316	408
Hardness	0.05	25	44
Total Solids	100	5890	9184
Dissolved Solids	0	5764	8852
Volatile Solids	0	682	1528
Color	5	100	500
Turbidity	11	12	15
Conductivity	880	5800	8200
Phenol	0.025	0.153	0.1355
pH	6.4	6.8	6.8
Mercury	-	-	<0.057
Manganese	0.04	0.08	0.32
Calcium	0.007	1.2	2.1
Iron	-	-	15
Nickel	-	-	1.4
Chromium	0.15	0.88	10
Zinc	0.06	0.02	4.5
Copper	0.04	0.1	3.0
Magnesium	0.02	5.0	11

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] Westinghouse module contained tubular polysulfone ultrafilter membranes.

[c] All results are in mg/ℓ, except for color (APHA units), turbidity (mg/ℓ SIO_2), conductivity (μmho/cm), pH (unitless), and mercury (μg/ℓ).

TABLE E-12. PERFORMANCE PARAMETERS OF SELAS AND WESTINGHOUSE MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #40

TYPE	Selas[a] Product	Westinghouse[b] Product	Selas/West Concentrate
SAMPLE NUMBER	674	675	676
DATE TAKEN	4/10/75	4/10/75	4/10/75
PARAMETER[c]			
COD	200	1220	1500
BOD	100	200	450
TOC	44	569	1192
Alkalinity	749	3833	316
Hardness	0.01	16	46
Total Solids	486	6884	10728
Dissolved Solids	486	6692	10366
Volatile Solids	144	864	1710
Color	0	200	300
Turbidity	0	12.0	14.0
Conductivity	730	6800	9600
Phenol	0.033	0.1245	0.140
pH	6.6	6.6	7.0
Mercury	-	-	<0.057
Manganese	0.04	0.12	0.32
Calcium	0.07	1.5	2.6
Iron	-	-	14
Nickel	-	-	1.1
Chromium	0.15	1.8	23
Zinc	0.02	0.03	3.6
Copper	0.1	0.1	2.9
Magnesium	0.02	6.8	9.2

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] Westinghouse module contained tubular polysulfone ultrafilter membranes.

[c] All results are in mg/ℓ, except for color (APHA units), turbidity (mg/ℓ SIO_2), conductivity (μmho/cm), pH (unitless), and mercury (μg/ℓ).

TABLE E-13. PERFORMANCE PARAMETERS OF WESTINGHOUSE MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #40

SAMPLE NUMBER	652	653
TYPE	Product	Concentrate
DATE TAKEN	4/3/75	4/3/75
PARAMETER[b]		
COD	800	1100
BOD	290	580
TOC	223	1256
Alkalinity	324	33
Hardness	19	43
Total Solids	5322	9250
Dissolved Solids	5220	8854
Volatile Solids	594	2142
Color	150	200
Turbidity	13.0	13.0
Conductivity	6500	8300
Phenol	0.111	0.065
pH	7.0	5.9
Mercury	<0.086	<0.043
Manganese	0.04	0.08
Calcium	1.1	1.7
Iron	-	8
Nickel	-	0.7
Chromium	1.0	15
Zinc	0.38	5.8
Copper	0.24	3.3
Magnesium	4.6	9.2

[a] Westinghouse module contained tubular polysulfone ultrafilter membranes.

[b] All results are in mg/ℓ, except for color (APHA units), turbidity (mg/ℓ SIO_2), conductivity (μmho/cm), pH (unitless), and mercury (μg/ℓ).

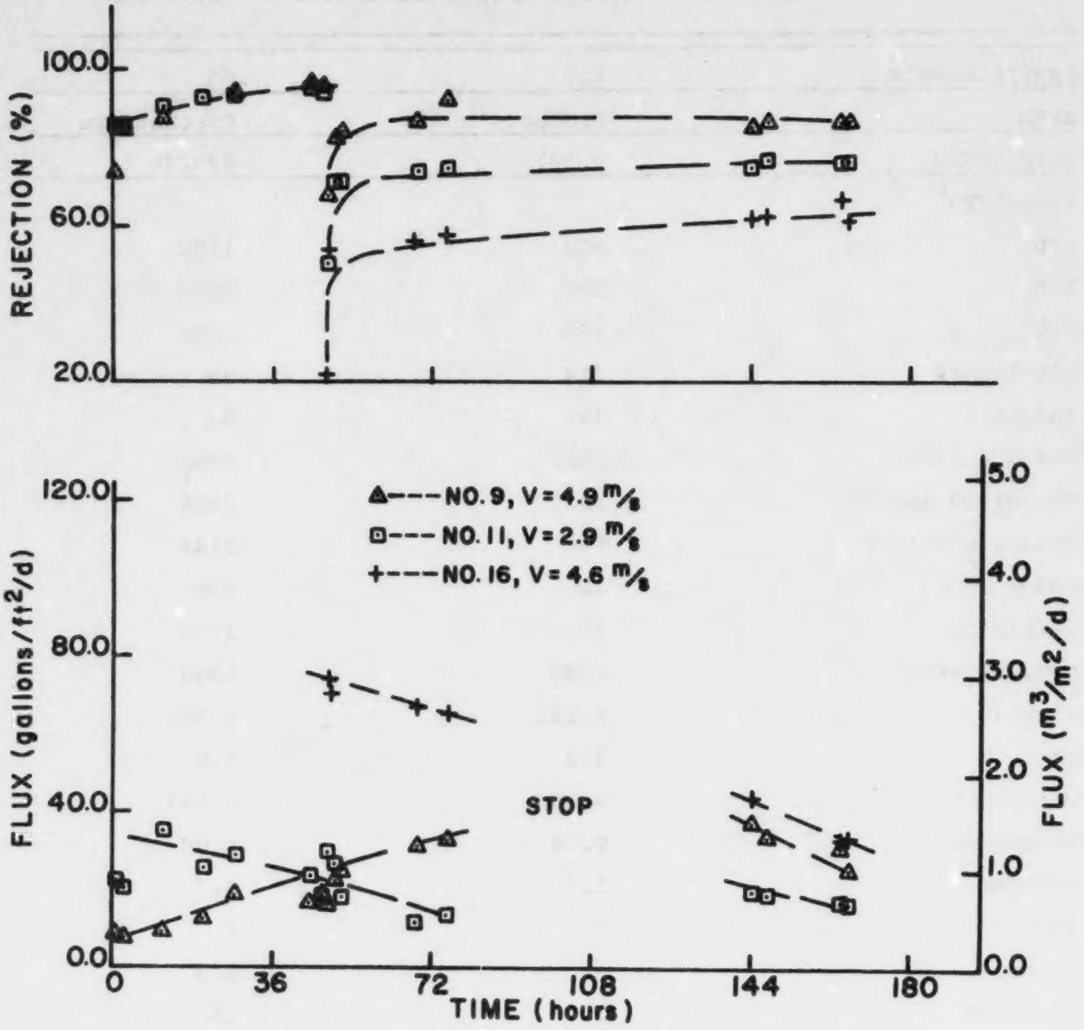

Figure E-3. Hyperfiltration of indigo waste at Plant #40 by Zr(IV)-PAA membranes on Selas ceramic supports. (P = 6.9 MPa (1000 psig); T = 40°C; pH = 8.6 - 11.0.)

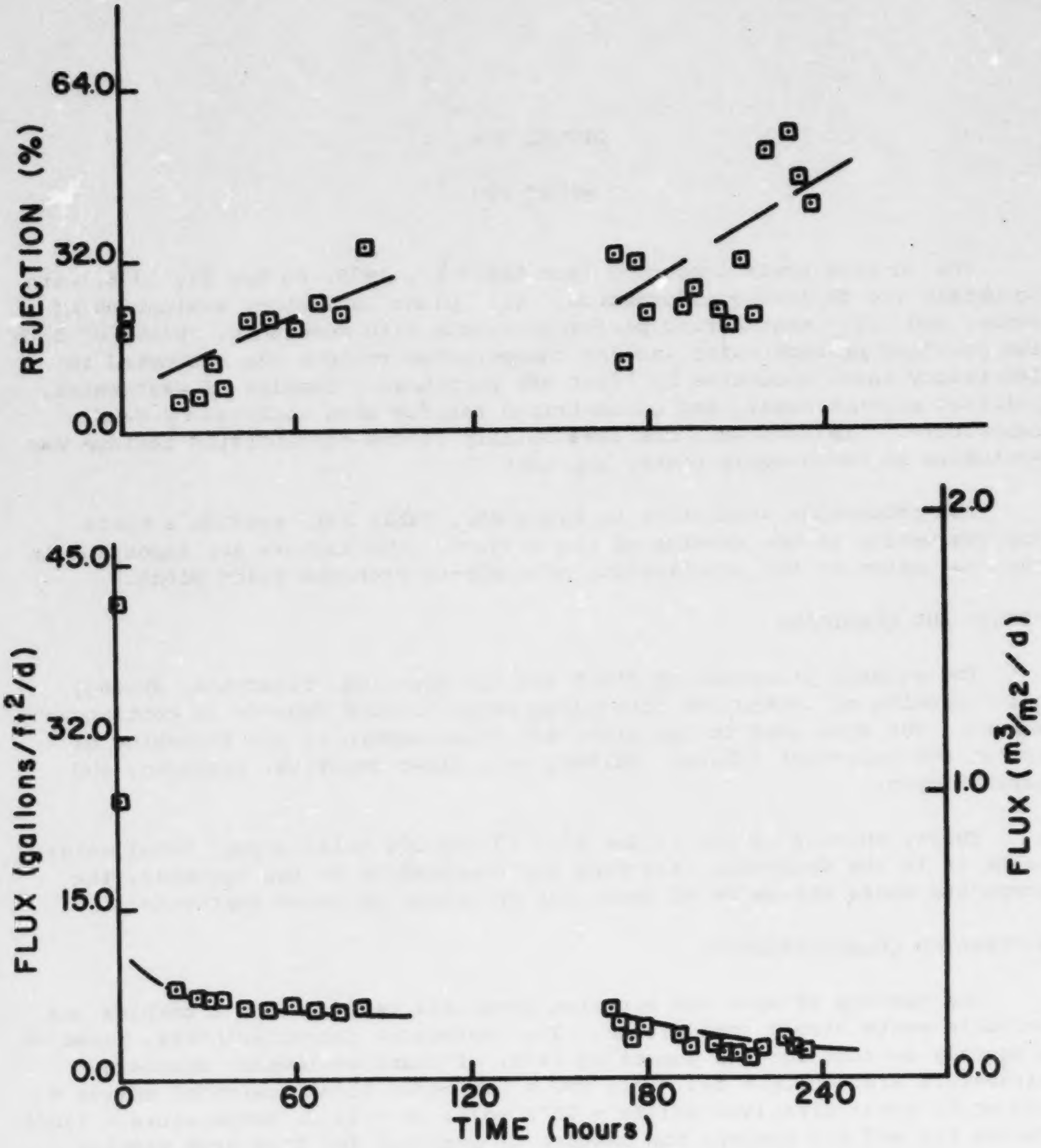

Figure E-4. **Hyperfiltration of combined effluent at Plant #40 by a Westinghouse module with a polysulfone membrane. (P = 2.1 MPa (300 psig); T = 40°C; pH = 7.7 - 9.5; reject flow rate = 8.3 - 13.6 dm^3/min (2.3 - 3.6 GPM); recovery = 75%.)**

APPENDIX F

PLANT #80

The on-site tests conducted from April 23, 1975, to May 21, 1975, were to obtain the following information: (1) plant laboratory evaluation of reuse, and (2) engineering performance data with membranes. Reuse of both the purified product water and the concentrated residue was evaluated in laboratory tests conducted by Plant #80 personnel. Samples of wastewater, purified product water, and concentrated residue were analyzed by Nardin Laboratory.[a] In addition, the treatability of the concentrated residue was evaluated in bench-scale tests, Appendix J.

The production parameters of Plant #80, Table F-1, provide a basis for evaluation of the results of the project. The factors are important in the evaluation of the practicality of scale-up from the pilot plant.

FIBERS AND CHEMICALS

The primary processes at Plant #80 are scouring, bleaching, dyeing, and finishing of cotton and cotton/polyester blended fabrics on continuous ranges. The dyes used in the plant are those common to the finishing of cotton and polyester fibers: sulfur, vat, fiber reactive, disperse, and napthol dyes.

Thirty percent of the 11,364 m^3/d (3,000,000 gallons/day) total water usage is in the dyehouse. Allowing for evaporation in the dyehouse, the composite waste stream is at least 30% by volume dyehouse wastewater.

WASTEWATER CHARACTERISTICS

The variety of dyes and scouring chemicals used produce a complex and variable waste stream composition. The wastewater characteristics, based on a monthly average for the summer of 1975, of plant wastewater discharge parameters are: BOD_5 = 349 mg/ℓ; COD = 645 mg/ℓ; total suspended solids = 193 mg/ℓ; total dissolved solids = 2473 mg/ℓ; pH = 11.8; temperature = 110°F. Tables F-2 and F-3 present the results of analyses for five grab samples

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[a] Division of Commonwealth Laboratory, Inc., Greenville, SC.

TABLE F-1. PLANT #80 PRODUCTION CAPACITY PARAMETERS

QUANTITIES USED	
Materials: cotton, cotton/polyester	
Water (total to plant), m^3/day	13,257
(gallons/day)	(3,500,000)
Water (to dyehouse), m^3/day	4,545
(gallons/day)	(1,200,000)
Dyes, kg/day	3,162
(pounds/day)	(6,973)
Auxiliary Chemicals, kg/day	29,035
(pounds/day)	(64,023)
Energy (for process steam), joules/day	4630×10^9
(Btu/day)	(4410×10^6)
UNIT COSTS	
Water, ¢/m^3	4
(\$/1000 gallons)	(0.15)
Fuel, ¢/10^7 joules	1.0
(\$/10^6 Btu)	(1.10)

obtained during the period of on-site testing. Plant #80 is classified as Subcategory 8, commission finishing.[a]

SCHEDULE AND PROCEDURE

Schedule

The mobile laboratory arrived at Plant #80 on April 23, 1975. The utilities were connected and the system was placed in operation on April 29. Initially, one-gallon (3.8ℓ) samples of purified product and concentrate were collected for reuse evaluation in the plant laboratory. The reuse samples were generated from the dyehouse wastewater and not from total plant composite wastewater. The ten-gallon (38ℓ) sample of concentrate for the treatability study was collected later from total plant composite wastewater.

The following is a list of events at Plant #80:

04/23 - Arrived from Plant #40.

04/29 - Generated reuse test samples utilizing Selas, Westinghouse polysulfone, and UOP spiral modules. Feed was composite effluent from the dyehouse only.

04/30 - Began parametric performance test with Selas and Westinghouse polysulfone membranes. Total plant effluent was feed.

05/06 - Installed DuPont's spiral polyamide membrane module.

05/07 - Removed DuPont module.

05/12 - Parametric performance test completed.

05/15 - Began special tests utilizing Selas, Westinghouse polysulfone, and Union Carbide's ultrafiltration modules.

05/20 - Tests completed.

05/21 - Departed to Plant #81.

Procedure

The membranes for evaluation were selected on the basis of availability and the characteristics of the wastewater. The wastewater was prefiltered through 25-micron cartridge filters prior to entering the mobile laboratory. The pH was adjusted when necessary to meet the membrane manufacturers specifications using sulfuric acid as the reagent. Figure F-1 shows schematically the equipment arrangement. Four module types were evaluated:

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[a] Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Textile Point Source Category. EPA-440/1-74-022-a, US Environmental Protection Agency, Washington, DC, 1974.

TABLE F-2. CHEMICAL ANALYSES OF PLANT #80 WASTEWATER[a]

SAMPLE NUMBER	J	E	A
DATE TAKEN		5/2/75	5/6/75
PARAMETER[b]			
COD	-	397	845
BOD	-	137	320
TOC	450	170	401
Alkalinity	-	1393	773
Hardness	17	7	12
Total Solids	-	1960	2208
Dissolved Solids	2069	1362	2175
Volatile Solids	-	365	575
Color	423	206	364
Turbidity	32	27	35
Conductivity	-	6100	5000
Phenol	-	-	-
pH	11.4	11.6	11.6
Mercury	0.057	0.057	-
Manganese	0.05	0.05	0.05
Calcium	1.8	2.5	1.5
Iron	0.15	0.15	0.15
Nickel	0.1	0.1	0.1
Chromium	0.15	0.15	0.15
Zinc	2.5	0.15	0.18
Copper	0.24	0.04	0.04
Magnesium	2.0	1.1	2.0

[a] Grab samples of combined plant effluent.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE F-3. CHEMICAL ANALYSES OF PLANT #80 WASTEWATER[a]

SAMPLE NUMBER	Q	K
DATE TAKEN	5/8/75	5/9/75
PARAMETER[b]		
COD	744	602
BOD	314	626
TOC	388	307
Alkalinity	1623	2540
Hardness	11	15
Total Solids	2830	3500
Dissolved Solids	2776	3579
Volatile Solids	660	810
Color	609	590
Turbidity	42	30
Conductivity	9000	11000
Phenol	-	-
pH	11.9	12.0
Mercury	-	-
Manganese	0.05	0.05
Calcium	2.7	2.8
Iron	0.15	0.15
Nickel	0.1	0.1
Chromium	0.15	0.15
Zinc	0.5	0.42
Copper	0.04	0.08
Magnesium	1.6	1.2

[a] Grab samples of combined plant effluent.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

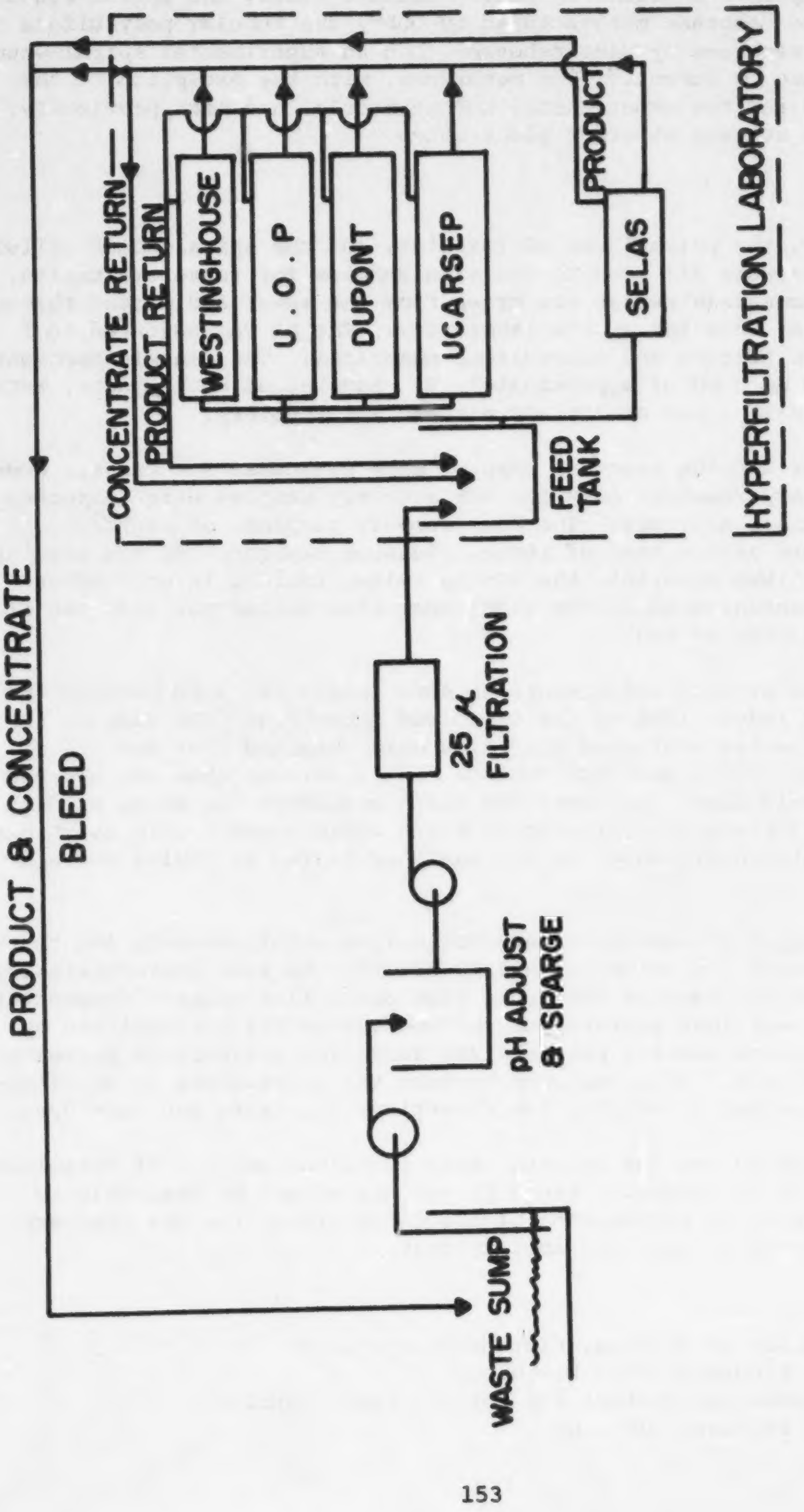
PRODUCT & CONCENTRATE BLEED
WASTE SUMP
pH ADJUST & SPARGE
25 μ FILTRATION
FEED TANK
CONCENTRATE RETURN
PRODUCT RETURN
WESTINGHOUSE
U. O. P
DUPONT
UCARSEP
SELAS
PRODUCT
HYPERFILTRATION LABORATORY

Figure F-1. Flow schematic for equipment set-up at Plant #80.

the dual-layer dynamic membrane on Selas[a] ceramic tubes, the spiral-wound cellulose acetate membrane manufactured by UOP[b], the tubular polysulfone ultrafiltration membrane by Westinghouse[c], and an experimental spiral-wound polyamide membrane by DuPont.[d] The membranes, with the exception of the Selas module #10 and the experimental DuPont module, had been previously exposed to waste streams at other plant sites.

REUSE

The dynamic, the polysulfone ultrafilter, and the spiral-wound cellulose acetate membranes were all used to generate samples for reuse evaluation. A sample of dyehouse wastewater was drawn from the sewer and pumped through a 25-micron filter into the mobile laboratory. The pH was adjusted to 5 for the cellulose acetate and polysulfone membranes. The dynamic membranes treated raw feed at a pH of approximately 9. Samples of both product water and concentrate were taken at 75% and also at 90% recovery.

Both the 75% and 90% recovery samples were evaluated for reuse. However, for budgetary reasons, only the 90% recovery samples were subjected to detailed chemical analyses. The 90% recovery samples, of course, represent the more severe test of reuse. Because membranes do not separate 100% of the dissolved material, the 10% by volume residue is only about eight times as concentrated as the plant composite wastewater (instead of the volumetric factor of ten).

The purified product water contains some chemicals, also because the membranes do not reject 100% of the dissolved materials. The samples of purified product water evaluated for reuse were obtained near the end of the concentration (90%), and thus contain more chemicals than the average product water would have. In fact, for these membranes the mixed product water from a full-scale hyperfiltration plant would contain only about one-third of the contaminants shown by the analyses listed in Tables F-4 and F-5.

The three types of membranes were not tested simultaneously and therefore did not process composite waste with exactly the same characteristics. The collection of the samples for reuse took about five hours. Concentrating the feed in the cellulose acetate/polysulfone system was accomplished by withdrawing cellulose acetate permeate and recycling polysulfone permeate back to the feed tank. This was done because the polysulfone is an ultrafilter and is expected to exhibit low rejections for salts and some dyes.

The concentrated residue in both cases contained about 0.5% dissolved solids and was highly colored. Since it may not always be desirable to attempt direct reuse or reclamation of the concentrate, the 90% recovery concentrate was used in the treatability tests.

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[a] Selas Corporation of America, Flotronics Division.

[b] Universal Oil Products, ROGA Division.

[c] Westinghouse Membrane Systems was sold to Union Carbide.

[d] E. I. DuPont, Permasep Division.

TABLE F-4. CHEMICAL ANALYSES OF WATER EVALUATED FOR REUSE[a] AT PLANT #80

(90% Water Recovery)

TYPE	Selas[b] Product	Selas Concentrate
SAMPLE NUMBER	711	712
DATE TAKEN	4/29/75	4/29/75
PARAMETER[c]		
COD	144	1128
BOD	52	300
TOC	22	282
Alkalinity	102	320
Hardness	1	70
Total Solids	634	4880
Dissolved Solids	634	4807
Volatile Solids	254	1380
Color	0	750
Turbidity	0	580
Conductivity	800	4600
Phenol	0.08	0.27
pH	9.0	8.0
Mercury	<0.001	<0.001
Manganese	0.13	0.07
Calcium	0.47	<0.01
Iron	2.48	3.80
Nickel	0.35	0.58
Chromium	0.11	0.44
Zinc	0.46	1.77
Copper	<0.1	0.58
Magnesium	1.57	1.43

[a] Reuse tests conducted in Plant #80 dye laboratory. Feed is combined effluent from dyehouse only.

[b] Selas module contained ceramic tubes with dynamic membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE F-5. CHEMICAL ANALYSES OF WATER EVALUATED FOR REUSE[a] AT PLANT #80
(90% Water Recovery)

TYPE	UOP[b] Product	Westinghouse[c] Product	UOP/West Concentrate
SAMPLE NUMBER	713	714	715
DATE TAKEN	4/29/75	4/29/75	4/29/75
PARAMETER[d]			
COD	208	268	468
BOD	105	105	120
TOC	42	61	78
Alkalinity	-52	-40	-85
Hardness	5	54	170
Total Solids	472	1900	4650
Dissolved Solids	472	1900	4645
Volatile Solids	96	260	370
Color	0	10	65
Turbidity	0	0	20
Conductivity	830	2250	5500
Phenol	0.055	0.07	0.03
pH	4.0	4.2	3.6
Mercury	<0.001	<0.001	<0.001
Manganese	0.05	0.12	<0.01
Calcium	<0.01	0.86	0.72
Iron	2.68	4.03	7.75
Nickel	0.41	0.64	0.76
Chromium	0.11	0.27	0.58
Zinc	1.09	6.58	9.91
Copper	0.15	0.42	1.78
Magnesium	2.10	1.55	1.62

[a] Reuse tests conducted in Plant #80 dye laboratory. Feed is combined effluent from dyehouse only.

[b] UOP module contained spiral-wound cellulose acetate membranes.

[c] Westinghouse module contained tubular polysulfone ultrafilter membranes.

[d] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

REUSE EVALUATION

Since the fibers processed by Plant #80 are cotton and polyester, the waste stream contains many chemicals associated with the scouring, desizing, and dyeing of these fibers and their blends. Because of this there was little likelyhood that chemicals could be recovered from the concentrated residue. The analyses results for the purified product and the concentrated residue at the 90% recovery level by the cellulose acetate and by the dynamic membranes are presented in Tables F-4 and F-5, respectively.

Reuse of Product Water

As a stringent test of reuse of the product water, the 90% recovery samples were evaluated. The analyses of the product water (Tables F-4 and F-5) indicate that the dynamic and cellulose acetate hyperfiltration membranes produce a product water with less organic and inorganic impurities than the polysulfone ultrafilter.

Laboratory evaluation for continuous range dyeings were run using product water to make up the dyebath. A control run was made using regular plant process water. A critical shade was chosen for each of the three dye systems: disperse/vat, disperse/sulfur, and disperse/reactive. The fabric used in each evaluation was 65/35 polyester/cotton poplin. The shades, with the dyes in the formulations, are shown in Table F-6.

The test dyeings were carried out in a laboratory range using standard operating procedures.

The reuse of product water in the dyebath did not effect these shades and was considered to be suitable for plant use. Shade variations were not more than expected when repeating the same dyeing with regular plant water.

Reuse of Concentrate

The concentrates were evaluated for content of reusable dyestuff. The evaluation consisted of running white fabric through the concentrate as the dye pad, with no addition of dye. All other chemicals were included. Cloth samples were taken after the thermosol to check for yellowing. The precipitation or agglomeration of dyestuff in the concentrate caused "dye spots." It is not known if special handling of samples would permit uniform dye application. Recycle of dyestuff in the concentrate was not considered practical based on these tests.

MEMBRANE PERFORMANCE

The engineering performance test of membranes was begun on April 30, 1975, utilizing the composite waste from the total plant as the feed. The pH was near 12 and was left unchanged for the first 82 hours of the test due to pH controller problems. The pH control was partially restored and pH was maintained at 7 - 10 for the remainder of the test. The Selas and Westinghouse polysulfone modules were used, but the UOP spiral module was removed from the system. The performance of the membranes was monitored by

TABLE F-6. PRODUCT WATER REUSE EVALUATION

Shade	Dyes in Formulation	
Blue	Poly. Blue D (1329)	2.90 g/ℓ
	Sody Rubine FGLS	0.50 g/ℓ
	Eastman Yellow GLSW	0.16 g/ℓ
	Sol. Blue FSBA	2.60 g/ℓ
	Sand Violet NBWM	0.60 g/ℓ
	May Olive TANM	0.60 g/ℓ
Brown	Poly. Blue D (1329)	40.00 g/ℓ
	Latyl Orange 2GFST	28.00 g/ℓ
	Sody Rubine FGLS	4.00 g/ℓ
	Sody Brown FLCL	66.00 g/ℓ
	Sody Tan RWCF	100.00 g/ℓ
Poppy Seed	Poly. Pink B	40.00 g/ℓ
	Eastman Yellow GLSW	7.50 g/ℓ
	Lev Red E2B	5.50 g/ℓ
	Lev Yellow EG	5.00 g/ℓ

periodic measurements of the product water flow rate through the membranes and the percentage conductivity rejection. The polysulfone and the dynamic Zr-PAA membranes were fed from a common tank. The volumetric recovery was allowed to rise to ∿88% by the withdrawal of Selas product water and was maintained at 88% throughout the test.

Dynamic Membrane

Four modules of Selas ceramic tubes with dynamic Zr-PAA membranes were evaluated. The performance is summarized in Figure F-2, a plot of flux and rejection throughout the test period. The characteristic initially rapid flux decine is evident. One of the modules, #10, was equipped with new membranes. Module #4 was equipped with an old membrane that had already been used at several other plant sites.

The erratic flux and rejection performance is probably due to the widely varying feed pH throughout the test. The flux used for design cost projections is 1.5 m/d (37 gallons/ft^2/d) at 45°C and 6.8 MPa (1000 psig).

While the flux generally declined, the conductivity rejection increased. Both phenomena may be the result of the formation of a fouling layer of residue formed on the membrane surface from the constituents in the wastewater.

The conductivity rejection is a measure of the separation or filtration of electrolytes by the membrane. The filtration efficiency for larger organic molecules is usually higher than for the electrolytes. Grab samples of the concentrate and the product water passing through the membranes were obtained during the 200-hour performance tests and analyzed to indicate the filtration efficiency for several constituents. The results of analyses for four pairs of samples are shown in Tables F-7 through F-10.

The 95 - 99% rejection of organics, indicated by COD, BOD, and color comparisons between the concentrate and product samples are greater than the conductivity rejections. The rejection of metals is very high, as indicated in all cases where results are significantly above the limit of detection.

Polysulfone Ultrafilter

The results of the performance test with the Westinghouse tubular ultrafilter are shown in Figure F-3. The unit was run at conditions specified by the manufacturer: pressure = 1.7 MPa (250 psig); temperature = 32 - 41°C; pH = 6.7 - 12; and reject flow rate = 13 - 14 dm^3/min (3.4 - 3.7 GPM). The high rejection and low fluxes shown in Figure F-3 are probably due to a combination of membrane compaction and the formation of a self-rejecting fouling layer. No washing procedures were attempted at Plant #80.

Tables F-7, F-8, and F-10 show analyses of Westinghouse product and concentrate samples enabling an evaluation of removal efficiency.

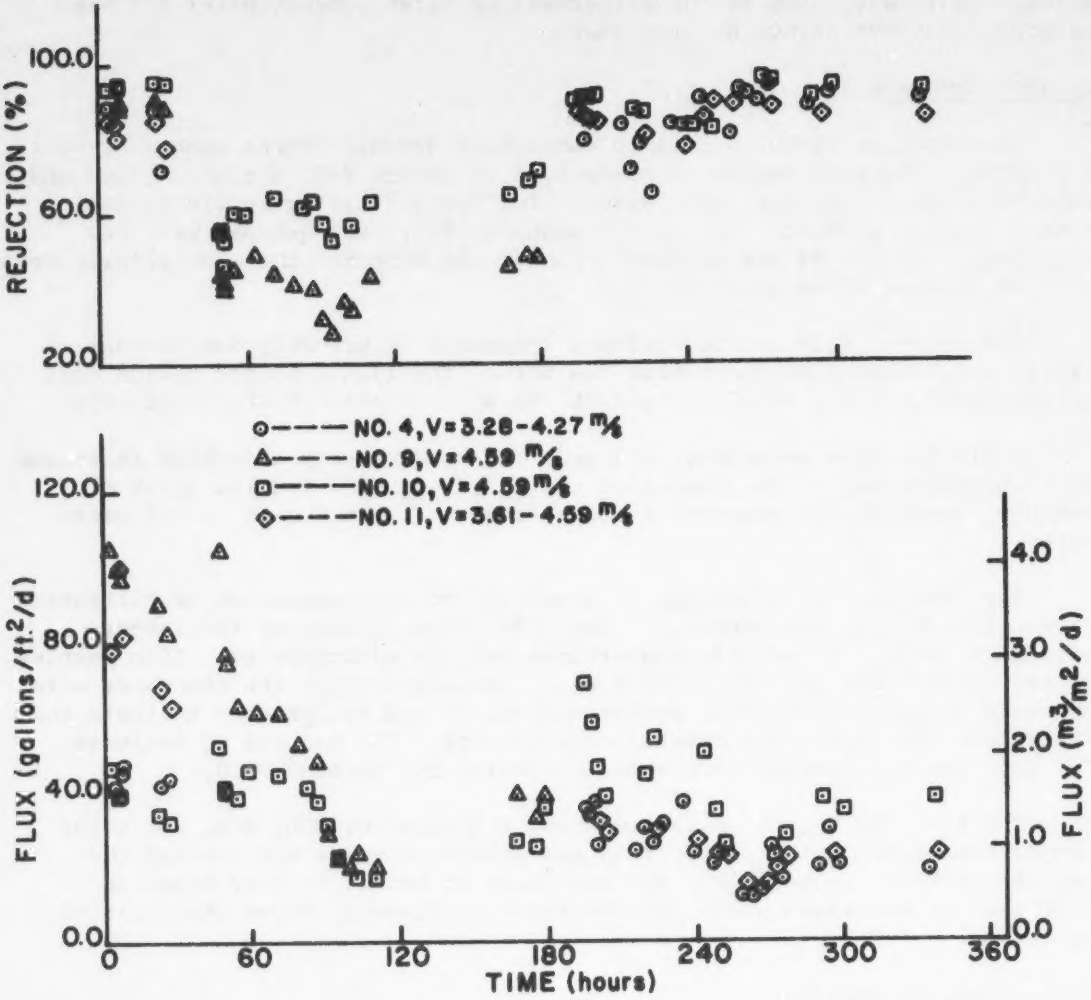

Figure F-2. Hyperfiltration of combined effluent at Plant #80 by Zr(IV)-PAA membranes on Selas ceramic supports. (P = 6.9 MPa (1000 psig); T = 46°C; pH = 5.5 - 12; recovery = 88%.)

TABLE F-7. PERFORMANCE PARAMETERS OF WESTINGHOUSE AND SELAS MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #80

TYPE	Westinghouse[a] Product	Selas[b] Product	West/Selas Concentrate
SAMPLE NUMBER	G	H	F
DATE TAKEN	5/1/75	5/1/75	5/1/75
PARAMETER[c]			
COD	426	51	1721
BOD	150	47	635
TOC	216	25	762
Alkalinity	1128	708	1158
Hardness	0	0	6
Total Solids	2223	900	3965
Dissolved Solids	1966	854	3705
Volatile Solids	525	120	1265
Color	64	1	1682
Turbidity	3.6	0.13	0.87
Conductivity	6000	3100	9000
Phenol	-	-	-
pH	11.6	11.4	11.6
Mercury	-	-	0.057
Manganese	-	-	0.05
Calcium	0.06	0.06	1.0
Iron	-	-	1.9
Nickel	-	-	0.1
Chromium	-	-	1.1
Zinc	-	-	3.1
Copper	0.04	0.04	0.92
Magnesium	0.02	0.02	3.8

[a] Westinghouse module contained tubular polysulfone ultrafilter membranes.

[b] Selas module contained ceramic tubes with dynamic membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE F-8. PERFORMANCE PARAMETERS OF SELAS AND WESTINGHOUSE MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #80

TYPE	Selas[a] Product	Westinghouse[b] Product	Selas/West Concentrate
SAMPLE NUMBER	C	D	B
DATE TAKEN	5/5/75	5/5/75	5/5/75
PARAMETER[c]			
COD	93	747	2803
BOD	48	344	1180
TOC	43	344	1338
Alkalinity	1055	1523	1600
Hardness	0.5	2	27
Total Solids	1685	4750	7465
Dissolved Solids	1416	2150	6888
Volatile Solids	473	2150	2535
Color	1	164	3409
Turbidity	0.17	0.5	0.33
Conductivity	5800	9000	10000
Phenol	-	-	-
pH	11.8	11.8	12.0
Mercury	-	-	-
Manganese	-	-	0.05
Calcium	0.06	0.18	2.3
Iron	-	-	2.5
Nickel	-	-	0.1
Chromium	0.15	0.15	1.4
Zinc	-	-	4.3
Copper	-	0.08	2
Magnesium	0.02	0.02	6.5

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] Westinghouse module contained tubular cellulose acetate membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE F-9. PERFORMANCE PARAMETERS OF SELAS AND DUPONT MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #80

TYPE	Selas[a] Product	DuPont[b] Product	Selas/DuPont Concentrate
SAMPLE NUMBER	O	P	N
DATE TAKEN	5/7/75	5/7/75	5/7/75
PARAMETER[c]			
COD	241	47	2776
BOD	121	22	1138
TOC	131	30	1058
Alkalinity	3	3	0
Hardness	3	0	100
Total Solids	1045	75	8830
Dissolved Solids	1054	68	8906
Volatile Solids	293	65	1950
Color	181	14	1571
Turbidity	0.14	0.69	23
Conductivity	1300	90	9000
Phenol	-	-	-
pH	7.2	8.8	6.4
Mercury	-	-	0.057
Manganese	-	-	0.05
Calcium	0.12	0.06	3.0
Iron	0.15	0.15	1.0
Nickel	0.1	0.1	0.1
Chromium	-	-	0.15
Zinc	-	-	4.4
Copper	0.12	0.04	0.92
Magnesium	0.22	0.02	7.6

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] DuPont module contained spiral-wound polyamide membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE F-10. PERFORMANCE PARAMETERS OF SELAS AND WESTINGHOUSE MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #80

TYPE	Selas[a] Product	Westinghouse[b] Product	Selas/West Concentrate
SAMPLE NUMBER	L	M	R
DATE TAKEN	5/9/75	5/9/75	5/9/75
PARAMETER[c]			
COD	81	913	2659
BOD	68	44	550
TOC	87	374	1121
Alkalinity	88	88	88
Hardness	0	43	149
Total Solids	605	6998	1243
Dissolved Solids	597	7376	12840
Volatile Solids	143	633	1830
Color	17	267	1161
Turbidity	0.17	1.5	24
Conductivity	950	9000	11000
Phenol	-	-	-
pH	10.5	9.75	9.2
Mercury	-	-	0.057
Manganese	-	-	0.15
Calcium	0.06	1.5	3.9
Iron	0.15	0.15	5.4
Nickel	0.1	0.1	0.1
Chromium	-	-	1.6
Zinc	-	-	5.7
Copper	0.04	0.08	1.2
Magnesium	0.02	4.2	10.2

[a] Selas modules contained ceramic tubes with dynamic membranes.

[b] Westinghouse modules contained tubular polysulfone ultrafilter membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

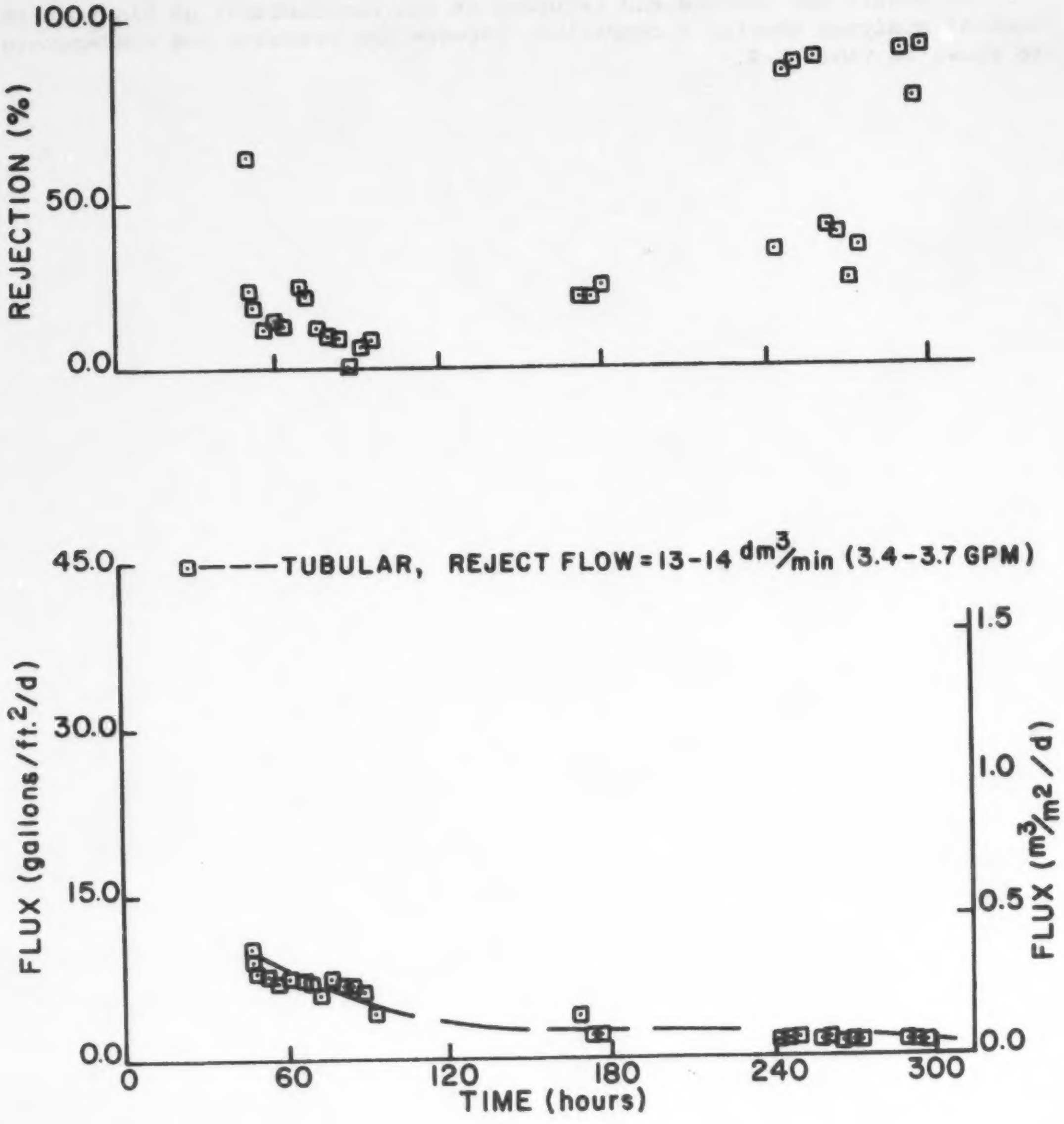

Figure F-3. Hyperfiltration of combined effluent at Plant #80 by tubular Westinghouse modules with a polysulfone membrane. (P = 1.7 MPa (250 psig); T = 32 - 41°C; pH = 6.7 - 12; recovery = 88%.)

Spiral Polyamide

During engineering performance tests, an experimental DuPont spiral-wound polyamide module was installed and run for about twenty-four hours.

The module was removed and returned to the manufacturer at his request. Chemical analyses showing a comparison between the permeate and concentrate are shown in Table F-9.

APPENDIX G

PLANT #81

The on-site tests conducted from May 21, 1975, to June 25, 1975, were to obtain the following information: (1) plant laboratory evaluation of reuse, and (2) engineering performance data with membranes. Reuse of both the purified product water and the concentrated residue was evaluated in laboratory tests conducted by Plant #81 personnel. The treatability of the concentrated residue was evaluated in bench-scale tests, Appendix J.

The production parameters of Plant #81, given in Table G-1, provide a basis for evaluation of the results of the project. The factors are important in the evaluation of the practicality of scale-up from the pilot plant.

FIBERS AND CHEMICALS

The wet finishing processes at Plant #81 involve the scouring, bleaching, dyeing, and finishing of cotton and cotton/polyester blended fabrics on continuous ranges. The principal classes of dyes are: sulfur, vat, fiber reactive, disperse, and napthol.

About 40% of the 30,682 m^3/d (8,100,000 gallons/day) total water usage is in the dyehouse. Allowing for evaporation in drying, the composite waste stream is at least 50% composed of scouring, bleaching, and desizing wastewater.

WASTEWATER CHARACTERISTICS

The variety of dyes and scouring chemicals used produce a complex and variable waste stream composition. The wastewater characteristics, based on a monthly average for the summer of 1975, of plant wastewater discharge parameters are: BOD_5 = 950 mg/ℓ; COD = 2050 mg/ℓ; total suspended solids = 150 mg/ℓ; total dissolved solids = 1900 mg/ℓ; pH = 11.0; temperature = 110°F. Table G-2 presents the results of analyses for a grab sample of composite wastewater (excluding printing operations) obtained during the period of on-site testing. Plant #81 is classified as Subcategory 8, complex manufacturing.[a]

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[a] Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Textile Point Source Category. EPA-440/1-74-022-a, US Environmental Protection Agency, Washington, DC, 1974.

TABLE G-1. PLANT #81 PRODUCTION CAPACITY PARAMETERS

QUANTITIES USED	
Materials: cotton, cotton/polyester	
Water (total to plant), m^3/day (gallons/day)	30,682 (8,100,000)
Water (to dyehouse), m^3/day (gallons/day)	12,121 (3,200,000)
Dyes, kg/day (pounds/day)	4,545 (10,000)
Auxiliary Chemicals, kg/day (pounds/day)	7,319 (16,100)
Energy (for process steam), joules/day (Btu/day)	12.8×10^{12} (12.2×10^{9})
UNIT COSTS	
Water, ¢/m^3 ($/1000 gallons)	5 (0.19)
Fuel Oil, ¢/10^7 joules ($/$10^6$ Btu)	1.1 (1.18)

SCHEDULE AND PROCEDURE

Schedule

The mobile laboratory arrived at Plant #81 on May 21, 1975. The utilities were connected and the system was placed in operation on May 27.

Initially, one-gallon (3.8ℓ) samples of purified product and concentrate were collected for reuse evaluation in the plant laboratory. A 19ℓ sample of concentrate was later collected for the treatability study.

The following is a list of events at Plant #81:

05/21 - Arrived from Plant #80.

05/27 - Reuse samples generated utilizing Selas Zr-PAA membrane modules. Composite effluent from plant was feed.

06/02 - Began parametric performance test utilizing Selas hyperfiltration modules, a Union Carbide ultrafilter, and a Westinghouse polysulfone ultrafilter. Feed was outflow from the steamer section of a continuous dye range.

06/04 - Use of Union Carbide and Westinghouse modules discontinued.

06/16 - Ended parametric performance test. Began special tests utilizing Selas Zr-sodium silicate modules.

06/23 - Ended special tests.

06/25 - Moved to Plant #82.

Procedure

The membranes for evaluation were selected based on availability and the characteristics of the wastewater. The wastewater was prefiltered through 25-micron cartridge filters prior to entering the mobile laboratory. The pH was adjusted when necessary to meet membrane manufacturer specifications. Figure G-1 shows schematically the equipment arrangement.

A new dual-layer dynamic membrane on Selas[a] ceramic tubes was used to generate the reuse samples from composite wastewater. Dynamic membranes that had been used previously at other mills were then installed and used to treat steamer seal water for 200 hours. A Union Carbide[b] tubular ultrafilter module with a type 3NJR membrane was evaluated briefly on the steamer seal wastewater.

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[a] Selas Corporation of America, Flotronics Division.
[b] Union Carbide Corporation, Membrane Systems Division.

TABLE G-2. CHEMICAL ANALYSES OF PLANT #81 WASTEWATER[a]

SAMPLE NUMBER	750
DATE TAKEN	5/26/75
PARAMETER[b]	
COD	2477
BOD	904
TOC	900
Alkalinity	385
Hardness	60
Total Solids	2713
Dissolved Solids	1900
Volatile Solids	611
Color	1000
Turbidity	275
Conductivity	1080
Phenol	990
pH	8.6
Mercury	-
Manganese	-
Calcium	2.52
Iron	1.13
Nickel	-
Chromium	0.002
Zinc	0.686
Copper	0.007
Magnesium	2.49

[a] Grab sample taken does not include effluent from printing operations.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

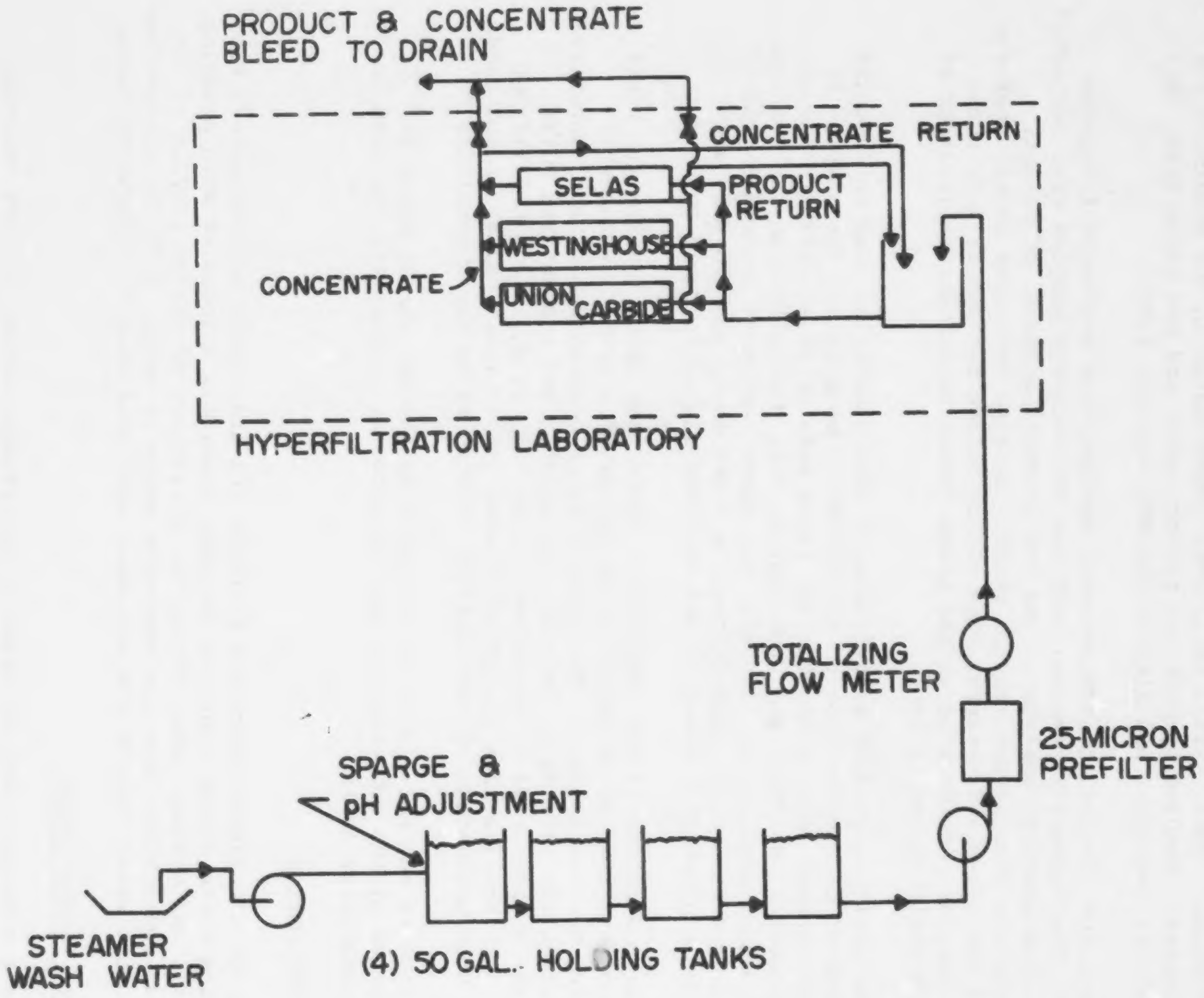
PRODUCT & CONCENTRATE
BLEED TO DRAIN
CONCENTRATE RETURN
SELAS
PRODUCT
RETURN
WESTINGHOUSE
CONCENTRATE
UNION CARBIDE
HYPERFILTRATION LABORATORY
TOTALIZING
FLOW METER
25-MICRON
PREFILTER
SPARGE &
pH ADJUSTMENT
STEAMER
WASH WATER
(4) 50 GAL. HOLDING TANKS

Figure G-1. Flow schematic for equipment set-up at Plant #81.

REUSE

The dual-layer dynamic membrane on Selas ceramic tubes was used to generate samples for reuse evaluation. Five barrels of composite wastewater, that did not include print shop wastewater, were prefiltered and introduced into the mobile laboratory without pH adjustment. The hyperfiltration was conducted until 90% (by volume) of the water was recovered as purified product water. Dyes, salts, etc., were concentrated in the remaining 10% of the water. Samples of both the product water and the concentrate were taken at 75% recovery, and also at the 90% recovery level.

Both the 75% and the 90% recovery samples were evaluated for reuse. However, for budgetary reasons, only the 90% recovery samples were subjected to detailed chemical analyses. The 90% recovery samples, of course, represent the more severe test of reuse. Because membranes do not separate 100% of the dissolved material, the 10% by volume residue is only about eight times as concentrated as the plant composite wastewater (instead of the volumetric factor of ten).

The purified product water contains some chemicals, also because the membranes do not reject 100% of the dissolved materials. The samples of purified product water evaluated for reuse were obtained near the end of the concentration (90%), and thus contain more chemicals than the average product water would have. In fact, for these membranes the mixed product water from a full-scale hyperfiltration plant would contain only about one-third the contaminants shown by the analyses listed in Table G-3.

The collection of the samples for reuse took about twenty-four hours. The concentration was accomplished by withdrawing product water while recycling the concentrate. The product water contained moderate concentrations of solids (500 mg/ℓ) and COD (328 mg/ℓ). The concentrate water contained a high level of dissolved solids (18,010 mg/ℓ) and COD (17,800 mg/ℓ). The total solids consisted of over 55% of ionic salts, as indicated by the high percentage of non-volatile substances in the concentrate.

Since it may not always be desirable to attempt direct reuse or reclamation of the concentrate, the 90% recovery concentrate was used in the treatability tests.

REUSE EVALUATION

Since the fibers processed by Plant #81 are cotton and polyester, the composite waste stream contains the many chemicals associated with scouring, desizing, and dyeing. Even though the likelyhood of direct recycle of the chemical concentrate from the composite waste is small, both the concentrate and product water from Zr-PAA membranes were evaluated in laboratory tests.

Reuse of Product Water

As a stringent test of reuse of the product water, the 90% recovery (least purified) samples were evaluated. The analyses of the product water

TABLE G-3. CHEMICAL ANALYSES OF WATER EVALUATED FOR REUSE[a] AT PLANT #81
(90% Water Recovery)

TYPE	Selas[b] Product	Selas Concentrate
SAMPLE NUMBER	755	756
DATE TAKEN	5/27/75	5/27/75
PARAMETER[c]		
COD	328	17800
BOD	$\geq$105	6200
TOC	-	-
Alkalinity	72	1300
Hardness	2	210
Total Solids	500	18010
Dissolved Solids	500	17810
Volatile Solids	250	10870
Color	0	4000
Turbidity	0	900
Conductivity	350	6800
Phenol	0.04	1.4
pH	8.6	7.1
Mercury	0.001	0.001
Manganese	0.01	3.97
Calcium	0.1	6.31
Iron	0.47	9.02
Nickel	0.2	2.12
Chromium	0.1	1.38
Zinc	0.07	7.76
Copper	0.1	1.59
Magnesium	0.01	11.36

[a] Reuse tests conducted in Plant #81 dye laboratory.

[b] Selas module contained ceramic tubes with dynamic membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

indicates that, in general, the COD and dissolved solids are more than expected for tap water. The concentration of metals is lower.

The product water was used in the plant laboratory with dispersed/fiber reactive dye mixtures and dispersed/vat dye mixtures. All reuse tests were with 65%/35% polyester/cotton fabric (128 x 72 - 50w 50f).

No problems were encountered with the use of the product water in these laboratory test dyeings. The fastness properties of the dyed fabric were the same as dyeings with normal plant water.

The specific procedures used by Plant #81 laboratory personnel are given here. For the reuse evaluation with the dispersed/fiber reactive dye formulation the procedure used is:

(1) Prepare dye formulation:

Remazol Yellow GL	16.48 gram/liter
Procion Blue H-7G	7.61 gram/liter
Dispersol Yellow D7G	6.96 gram/liter
Latyl Blue BG	24.31 gram/liter
Foron Yellow Brown BM	32.00 gram/liter
Astrotherm AM	7.50 gram/liter

(2) Pad and dry.
(3) Thermosol in roller oven.
(4) Pad through reduction bath.
(5) Pad through oxidation bath.
(6) Wash in Igepon solution T-33.
(7) Rinse and dry.

For the reuse evaluation with the dispersed/vat dye formulation, the procedure used is:

(1) Prepare dye formulation:

Yellow Ester Oquinon 3JLLN	6.42 gram/liter
Rubine Eastman RL 5W 50% PS	1.20 gram/liter
Blue Foron BGL Pst	1.32 gram/liter
Brown Veranthrene GAP	4.54 gram/liter
Olive Calcoloid TCM Pst	1.14 gram/liter
Orange Instravat 5G	0.62 gram/liter
Astrotherm AM	7.50 gram/liter

(2) Pad and dry.
(3) Thermosol.
(4) Run through chemical pad.
(5) Steam.
(6) Soap.
(7) Rinse.
(8) Dry on dry cans.

Reuse of Concentrate

The concentrates resulting from both 75% and 90% recoveries were evaluated in the laboratory for a pad-dry-thermosol-steam procedure. The composite waste concentrate was not suitable. With all dyebaths tested dinginess and slight discoloration were noted on the blank dyeing sequences: sulfur, brine (reactive), and caustic/hydrosulfite. No value could be observed from reuse of the concentrate obtained from the composite waste stream.

It is possible, when the wastewater and chemicals are recovered by hyperfiltration, to change the process to (1) achieve faster dyeing cycles, and/or (2) to eliminate the need for some auxiliary chemicals. For example, with direct dyeing of cellulose, salt can be eliminated by using higher concentrations of dye in the dyebath. Excess dyestuffs will be recovered by the membranes for reuse in the next cycle. Depending on the amount of fiber dyed and range of colors, this modification may or may not be practical. Water, chemicals, and energy requirements will play a major role in the selection of dyeing processes used in the future.

MEMBRANE PERFORMANCE

The Zr-PAA dynamic membranes were operated on pretreated steamer vapor seal wastewater (Table G-4) for 200 hours beginning on June 2, 1975. Union Carbide's tubular module with type 3NJR membranes was also briefly evaluated. The performance of the membranes was monitored by periodic measurements of the product water flow rate through the membranes and the percentage conductivity rejection.

The incoming feed was neutralized to pH = 7 - 8 with sulfuric acid and controlled at that level throughout most of the test. The chemical analyses of five grab samples taken over the ten-day test period are presented in Tables G-5 and G-6. Neutralization was discontinued and the pH rose to the untreated value of near 11 during the latter portion of the test. Table G-4 shows the analyses of a sample of feed taken after neutralization and 25-micron prefiltration. A volumetric recovery of 80% was achieved by the withdrawal of product water and was maintained at 80% throughout the 200-hour test.

Dynamic Membrane

Three modules of Selas ceramic tubes with dynamic Zr-PAA membranes were evaluated. The performance is summarized in Figure G-2, a plot of flux and rejection for the test period. The flux declined throughout the test period with the greatest decline shown in the earlier portion of the test. Rejection increased throughout the test. Low conductivity rejection is accounted for by high feed conductivities (25,000 to 40,000 μmho/cm). The increase in rejection with time might be explained by the dynamic formation of a "membrane" from constituents of the feed stream. Module #4 contained older membranes (8,000 hours) that had been used at several other plants. This older membrane exhibited a lower initial flux.

The conductivity rejection is a measure of the separation or filtration of electrolytes by the membrane. The filtration efficiency for larger organic molecules is usually higher than for the electrolytes. Grab samples of the feed to the membrane and the product water passing through the

TABLE G-4. CHEMICAL ANALYSES OF WASTE FROM THE STEAMER VAPOR SEAL, RANGE 116, TREATED[a] FOR MEMBRANE PERFORMANCE AT PLANT #81

SAMPLE NUMBER	764
DATE TAKEN	6/4/75
PARAMETER[b]	
COD	560
BOD	131
TOC	150
Alkalinity	133
Hardness	100
Total Solids	12732
Dissolved Solids	11350
Volatile Solids	180
Color	3000
Turbidity	6
Conductivity	18000
Phenol	0.460
pH	7.6
Mercury	-
Manganese	-
Calcium	1.48
Iron	1.61
Nickel	-
Chromium	0.005
Zinc	0.653
Copper	0.97
Magnesium	1.75

[a] Grab sample after 25-micron prefiltration, followed by neutralization to pH ∿ 7.5.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE G-5. CHEMICAL ANALYSES OF WASTE[a] FROM THE STEAMER VAPOR SEAL, RANGE 116, AT PLANT #81

SAMPLE NUMBER	757	763
DATE TAKEN	6/2/75	6/4/75
PARAMETER[b]		
COD	613	960
BOD	996	205
TOC	140	265
Alkalinity	338	552
Hardness	34	300
Total Solids	19305	16597
Dissolved Solids	19122	16262
Volatile Solids	129	116
Color	1000	17500
Turbidity	3	7
Conductivity	540	25200
Phenol	31.60	220
pH	11.6	12.0
Mercury	-	-
Manganese	-	-
Calcium	1.48	1.52
Iron	1.13	0.968
Nickel	-	-
Chromium	0.002	0
Zinc	0.0057	0.0041
Copper	0.009	0.006
Magnesium	1.39	1.05

[a] Grab samples.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE G-6. CHEMICAL ANALYSES OF WASTE[a] FROM THE STEAMER VAPOR SEAL, RANGE 116, AT PLANT #81

SAMPLE NUMBER	769	774	781
DATE TAKEN	6/6/75	6/10/75	6/12/75
PARAMETER[b]			
COD	848	896	912
BOD	13	140	367
TOC	135	180	180
Alkalinity	604	2543	2081
Hardness	80	100	100
Total Solids	23429	6627	6226
Dissolved Solids	20195	6327	6063
Volatile Solids	147	100	105
Color	2000	1000	900
Turbidity	1	9	11
Conductivity	32400	9000	9000
Phenol	-	0	0
pH	11.5	12.2	12.1
Mercury	-	-	-
Manganese	-	-	-
Calcium	1.70	0.933	0.933
Iron	1.45	0.806	0.806
Nickel	-	-	-
Chromium	0.003	0	0
Zinc	0.082	0.082	0.007
Copper	0.097	0	0.002
Magnesium	0.695	1	1.07

[a] Grab samples.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

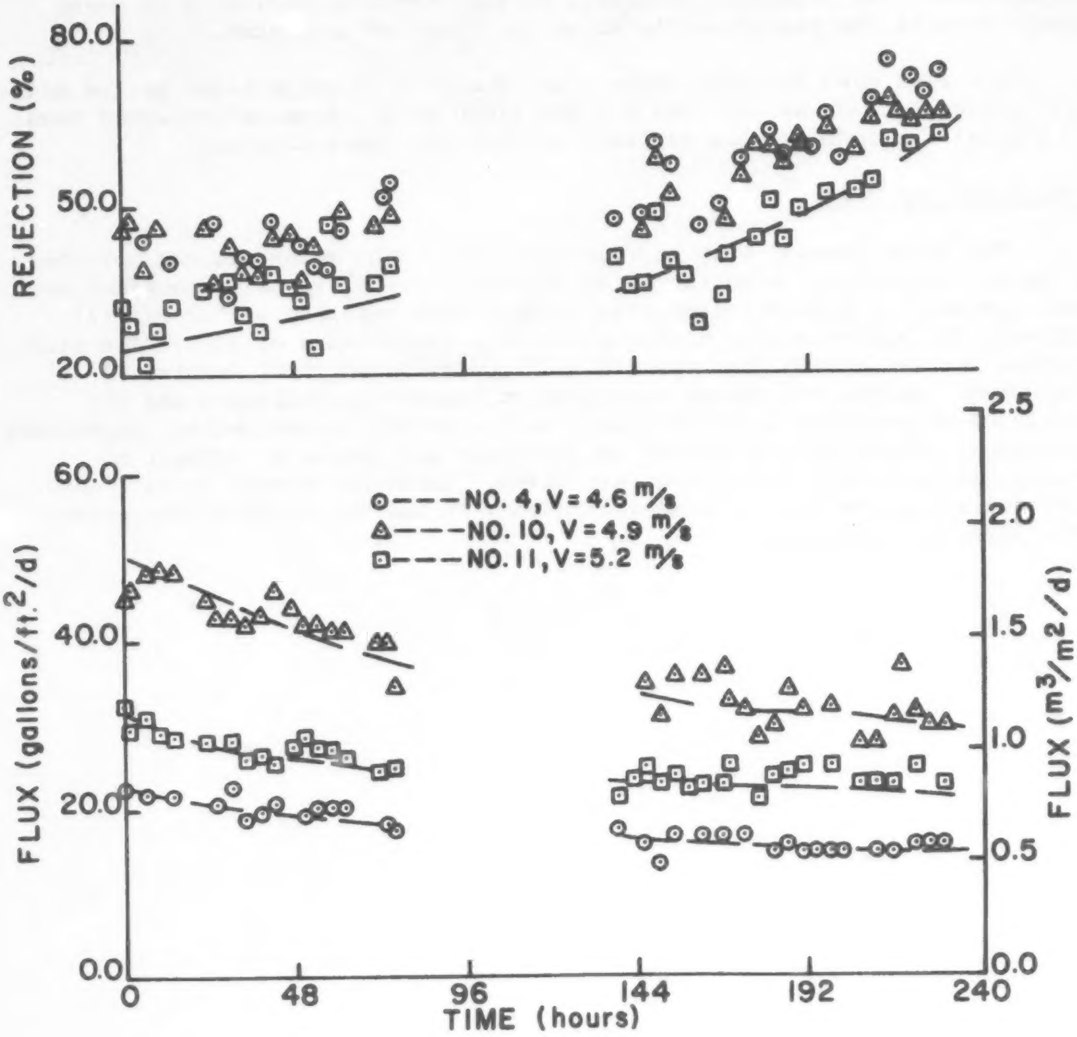

Figure G-2. Hyperfiltration of steamer seal waste at Plant #81 by Zr(IV)-PAA membranes on Selas ceramic supports. (P = 6.9 MPa (1000 psig); T = 51°C; pH = 6.8 - 11; recovery = 80%.)

membranes were obtained during the 200-hour performance tests and analyzed to indicate the filtration efficiency for several constituents. The results of analyses for three pairs of samples are shown in Tables G-7, G-8, and G-9.

The rejection of organics, indicated by COD, BOD, and color comparisons between the concentrate and product samples are greater than the conductivity rejections. The rejection of metals is very high, as indicated in cases where results are significantly above the limit of detection.

The flux used for full-scale plant design cost projections is 1.4 m/d (35 gallons/ft^2/d) at 43°C and 6.8 MPa (1000 psig), a value estimated from the brief run on composite effluent to generate reuse samples.

Union Carbide 3NJR

The Union Carbide unit equipped with type 3NJR membranes was operated, briefly, in parallel with the Selas modules. The previously unexposed unit was operated at 0.69 MPa (100 psig) with a feed velocity of 5.2 m/s (17 ft/sec) for approximately twelve hours at a temperature of 40°C. The flux showed little decline from the 4.0 m/d (100 gallons/ft^2/d) initially observed. During its operation a product sample was collected and its analyses is included in Table G-10, along with the corresponding concentrate analyses. These results cannot be explained and should be subject to verification before conclusions are drawn. These are simple measurements, and due to limitations of time and budget, it was not possible to resolve the apparent ambiguities.

TABLE G-7. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #81[b]

SAMPLE NUMBER	765	766
TYPE	Product	Concentrate
DATE TAKEN	6/5/75	6/5/75
PARAMETER[c]		
COD	272	933
BOD	39	644
TOC	47	400
Alkalinity	98	259
Hardness	22	400
Total Solids	9623	19001
Dissolved Solids	9381	18453
Volatile Solids	40	213
Color	2000	7500
Turbidity	8	24
Conductivity	14400	21600
Phenol	150.4	141
pH	7.9	8.0
Mercury	-	-
Manganese	-	-
Calcium	1.24	1.52
Iron	1.13	4.35
Nickel	-	-
Chromium	0	0.129
Zinc	0.408	3.57
Copper	0.002	0.388
Magnesium	1.52	2.22

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] Feed is filtered, neutralized waste from the steamer vapor seal, Range 116.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE G-8. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #81[b]

SAMPLE NUMBER	770	771
TYPE	Product	Concentrate
DATE TAKEN	6/9/75	6/9/75
PARAMETER[c]		
COD	168	1171
BOD	35	295
TOC	32	420
Alkalinity	53	173
Hardness	16	200
Total Solids	9910	19543
Dissolved Solids	9010	18888
Volatile Solids	47	77
Color	40	30000
Turbidity	6	33
Conductivity	10800	21600
Phenol	30	51
pH	7.5	7.4
Mercury	-	-
Manganese	-	-
Calcium	1.41	2.52
Iron	0.968	0.790
Nickel	-	-
Chromium	0	0.307
Zinc	0.571	5.63
Copper	0.002	0.437
Magnesium	1.73	2.29

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] Feed is filtered, neutralized waste from the steamer vapor seal, Range 116.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE G-9. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #81[b]

SAMPLE NUMBER	777	778
TYPE	Product	Concentrate
DATE TAKEN	6/11/75	6/11/75
PARAMETER[c]		
COD	120	1200
BOD	41	618
TOC	32	440
Alkalinity	245	1695
Hardness	10	200
Total Solids	9837	21336
Dissolved Solids	7824	20350
Volatile Solids	1032	306
Color	20	8500
Turbidity	5	30
Conductivity	9000	21600
Phenol	70.6	0
pH	11.1	10.7
Mercury	-	-
Manganese	-	-
Calcium	0.252	2.81
Iron	0.654	5.97
Nickel	-	-
Chromium	0	0.153
Zinc	0.082	2.86
Copper	0	0.243
Magnesium	0.134	1.99

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] Feed is filtered, neutralized waste from the steamer vapor seal, Range 116.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE G-10. PERFORMANCE PARAMETERS OF SELAS AND UCC MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #81

TYPE	Selas[a] Product	Selas/UCC Concentrate	UCC[b] Product
SAMPLE NUMBER	759	760	761
DATE TAKEN	6/3/75	6/3/75	6/3/75
PARAMETER[c]			
COD	720	1160	1944
BOD	39	428	636
TOC	50	330	280
Alkalinity	260	314	301
Hardness	14	360	200
Total Solids	14664	24759	22464
Dissolved Solids	13987	23853	22100
Volatile Solids	62	804	356
Color	1000	1000	2500
Turbidity	4	18	9
Conductivity	10800	10800	10800
Phenol	201.6	241.2	-
pH	8.6	8.1	8.8
Mercury	-	-	-
Manganese	-	-	-
Calcium	1.26	2.07	2.15
Iron	0.968	2.90	3.55
Nickel	-	-	-
Chromium	0.003	0.172	0.067
Zinc	0.0057	1.64	0.753
Copper	0.003	0.397	0.175
Magnesium	1.24	2.01	1.95

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] UCC module contained type 3NJR membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

APPENDIX H

PLANT #82

The on-site tests conducted from June 25, 1975, to July 30, 1975, were to obtain the following information: (1) plant laboratory evaluation of reuse, and (2) engineering performance data with membranes. Reuse of both the purified product water and the concentrated residue was evaluated in laboratory tests conducted by Plant #82 personnel. Samples of wastewater, purified product water, and concentrated residue were analyzed by Nardin Laboratory.[a] In addition, the treatability of the concentrated residue was evaluated in bench-scale tests, Appendix J.

The production parameters of Plant #82, Table H-1, provide a basis for evaluation of the results of the project. The factors are important in the evaluation of the practicality of scale-up from the pilot plant.

FIBERS AND CHEMICALS

Plant #82 is presently operated to scour, bleach, dye, and finish cotton and cotton/polyester blended fabrics. The chemicals and dyes used by the plant are those which are common to the finishing of cotton and polyester fibers: sulfur, vat, fiber reactive, disperse, and napthol dyes.

Ninety percent of the 6,629 m^3/d (1,750,000 gallons/day) total water usage is in the plant. Allowing for evaporation in drying, the composite waste stream is at least 85% by volume plant wastewater.

WASTEWATER CHARACTERISTICS

The variety of dyes and scouring chemicals used produce a complex and variable waste stream composition. The wastewater characteristics, based on a monthly average for the summer of 1975, of plant wastewater discharge parameters are: BOD_5 = 350 mg/ℓ; COD = 570 mg/ℓ; total suspended solids = 346 mg/ℓ; total dissolved solids = 2230 mg/ℓ; pH = 8.5; temperature = 90°F. Tables H-2 and H-3 present the results of analyses for six grab samples

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[a] Division of Commonwealth Laboratory, Inc., Greenville, SC.

TABLE H-1. PLANT #82 PRODUCTION CAPACITY PARAMETERS

QUANTITIES USED	
Materials: cotton, cotton/polyester	
Water (total to plant), m^3/day	6,629
(gallons/day)	(1,750,000)
Water (to dyehouse), m^3/day	4,545
(gallons/day)	(1,200,000)
Dyes, kg/day	537
(pounds/day)	(1,184)
Auxiliary Chemicals, kg/day	8,224
(pounds/day)	(18,134)
Energy (for process steam), joules/day	1327×10^9
(Btu/day)	(1264×10^6)
UNIT COSTS	
Water, ¢/m^3	-
(\$/1000 gallons)	-
Fuel Oil, ¢/10^7 joules	1.5
(\$/10^6 Btu)	(1.65)

TABLE H-2. CHEMICAL ANALYSES OF PLANT #82 WASTEWATER[a]

SAMPLE NUMBER	800	805	809
DATE TAKEN	7/16/75	7/17/75	7/19/75
PARAMETER[b]			
COD	717	897	196
BOD	144	36	3
TOC	510	270	8
Alkalinity	77	1270	57
Hardness	12	13.6	5
Total Solids	2515	2417	156
Dissolved Solids	2364	2390	152
Volatile Solids	423	544	117
Color	170	180	30
Turbidity	50	80	10
Conductivity	3100	6300	135
Phenol	0.04	0.11	0.03
pH	6.3	10.8	7.1
Mercury	-	-	-
Manganese	0.07	0.07	0.07
Calcium	1.90	3.62	0.90
Iron	0.89	0.17	0.10
Nickel	0.20	0.20	0.20
Chromium	0.10	0.10	0.10
Zinc	0.28	0.05	0.02
Copper	0.25	0.25	0.25
Magnesium	1.27	0.49	0.17

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE H-3. CHEMICAL ANALYSES OF PLANT #82 WASTEWATER[a]

SAMPLE NUMBER	810	815	816
DATE TAKEN	7/22/75	7/23/75	7/25/75
PARAMETER[b]			
COD	592	800	310
BOD	70	193	59
TOC	116	250	210
Alkalinity	1260	1930	91
Hardness	8	3	8
Total Solids	2807	4183	928
Dissolved Solids	2790	3976	736
Volatile Solids	1232	743	323
Color	40	240	120
Turbidity	30	35	40
Conductivity	6900	8000	1100
Phenol	0.02	0.02	0.045
pH	10.9	11.2	7.0
Mercury	-	-	-
Manganese	0.07	0.07	0.07
Calcium	1.88	1.39	2.16
Iron	0.14	0.24	0.97
Nickel	0.20	0.20	0.20
Chromium	0.10	0.10	0.10
Zinc	0.14	0.09	0.91
Copper	0.25	0.25	0.29
Magnesium	1.12	0.40	0.89

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

obtained during the period of on-site testing. Plant #82 is classified as Subcategory 8, commissioned finishing.[a]

SCHEDULE AND PROCEDURE

Schedule

Testing was begun on July 9, 1975. One-gallon (3.8ℓ) samples of purified product and concentrate were collected for reuse evaluation in the plant laboratory. A 38ℓ sample of concentrate was later collected for the biological treatability study.

The following is a summary of events at Plant #82:

06/25 - Arrived from Plant #81; utilities connected.

07/16 - Began parametric performance test with UOP and Selas modules.

07/17 - Reuse test samples generated.

07/29 - Parametric performance test completed.

07/30 - Departed to Plant #83.

Procedure

The membranes for evaluation were selected based on availability and the characteristics of the wastewater. The wastewater was prefiltered through 25-micron cartridge filters prior to entering the mobile laboratory. The pH was adjusted when necessary to meet membrane manufacturer specifications. Figure H-1 shows schematically the equipment arrangement. Two types of membranes were employed in these tests: the UOP[b] spiral-wound cellulose acetate membrane and the dual-layer dynamic membrane on the Selas[c] ceramic tubes.

REUSE

All types of membranes were used to generate samples for reuse evaluation. A sample of composite wastewater was drawn from the plant sewer, and pumped through a 25-micron filter into the mobile laboratory. The hyperfiltration was conducted until 90% (by volume) of the water was recovered as purified product water. Dyes, salts, etc., were concentrated in the remaining 10% of the water. Samples of both the product water and the concentrate were taken at 75% recovery, and also at the 90% recovery level.

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[a] Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Textile Point Source Category. EPA-440/1-74-022-a, US Environmental Protection Agency, Washington, DC, 1974.

[b] Universal Oil Products, ROGA Division.

[c] Selas Corporation of America, Flotronics Division.

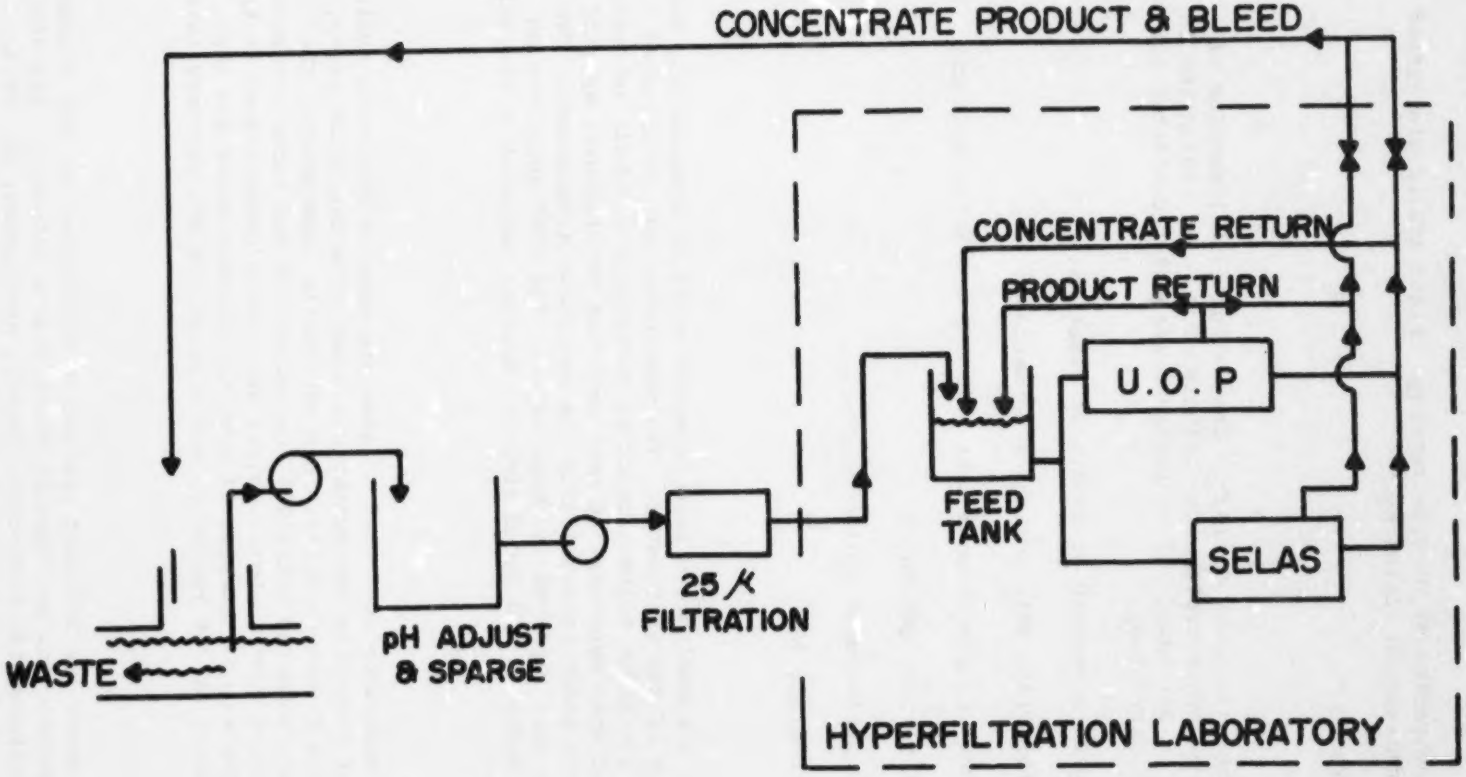
CONCENTRATE PRODUCT & BLEED
CONCENTRATE RETURN
PRODUCT RETURN
U.O.P
SELAS
FEED TANK
HYPERFILTRATION LABORATORY
25 μ FILTRATION
pH ADJUST & SPARGE
WASTE

Figure H-1. Flow schematic for equipment set-up at Plant #82.

Both the 75% and the 90% recovery samples were evaluated for reuse. However, for budgetary reasons, only the 90% recovery samples were subjected to detailed chemical analyses. The 90% recovery samples, of course, represent the more severe test of reuse. Because membranes do not separate 100% of the dissolved material, the 10% by volume residue is only about eight times as concentrated as the plant composite wastewater (instead of the volumetric factor of ten).

The purified product water contains some chemicals, also because the membranes do not reject 100% of the dissolved materials. The samples of purified product water evaluated for reuse were obtained near the end of the concentration (90%), and thus contain more chemicals than the average product water would have. In fact, for these membranes the mixed product water from a full-scale hyperfiltration plant would contain only about one-third the contaminants shown by the analyses listed in Table H-4.

The two types of membranes were tested simultaneously and therefore processed composite waste with exactly the same characteristics. The collection of samples for reuse took about eight hours. The concentration was accompliahed by withdrawing Selas product while recycling the UOP product to the concentrate tank.

The product water contained high concentrations of solids (1140 and 82 mg/ℓ) and COD (94 and 96 mg/ℓ). This was expected because of the high concentrations in the waste stream and was not indicative of poor membrane performance.

The concentrate water was very strong, containing 10710 mg/ℓ total solids, and 3620 mg/ℓ of COD. The total solids are mostly salts as indicated by the high percentage of non-volatile substances in the concentrate. This data agrees with the percentage of non-volatile salt found in the plant effluent.

Since it may not always be desirable to attempt direct reuse or reclamation of the concentrate, the 90% recovery concentrate was used in the treatability tests.

REUSE EVALUATION

Since the fibers processed by Plant #82 are cotton and polyester, the waste stream contains the many chemicals associated with the scouring, desizing, and dyeing of these fibers and their blends. Because of this there was little likelyhood that chemicals could be recovered from the concentrated residue. There is the possibility of recovering chemicals from isolated process waste streams. The analyses results for the purified product water and the concentrated residue from both the cellulose acetate and the dynamic membranes are presented in Table H-4.

Reuse of Product Water

As a stringent test of the reuse of the product water, the 90% recovery samples were evaluated. The analyses of the product water indicates that,

TABLE H-4. CHEMICAL ANALYSES OF WATER EVALUATED FOR REUSE[a] AT PLANT #82

(90% Water Recovery)

TYPE	Selas[b] Product	Selas/UOP Concentrate	UOP[c] Product
SAMPLE NUMBER	796	797	798
DATE TAKEN	7/16/75	7/16/75	7/16/75
PARAMETER[d]			
COD	94	3620	66
BOD	11	760	26
TOC	17.4	729	14.4
Alkalinity	31	170	27
Hardness	2	140	1
Total Solids	1140	10710	82
Dissolved Solids	1135	10683	82
Volatile Solids	130	1440	38
Color	5	450	0
Turbidity	8	70	0
Conductivity	1300	14500	65
Phenol	0.015	0.09	0.07
pH	618	616	615
Mercury	<0.001	<0.001	<0.001
Manganese	<0.01	0.39	<0.01
Calcium	<0.01	2.74	<0.01
Iron	0.17	11.74	0.66
Nickel	0.09	1.41	<0.01
Chromium	<0.01	0.33	0.04
Zinc	0.18	18.32	0.33
Copper	0.04	2.01	0.03
Magnesium	0.04	12.23	0.04

[a] Reuse tests conducted in Plant #82 dye laboratory.

[b] Selas module contained ceramic tubes with dynamic membranes.

[c] UOP module contained spiral-wound cellulose acetate membranes.

[d] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

in general, the COD and dissolved solids are much more than expected for tap water.

All of the purified product water generated by the mobile laboratory at Plant #82 was evaluated in the plant laboratory and found suitable for reuse in the plant.

The product water was used in the laboratory with acid and disperse dyes to dye (1) a blue shade on a 70% dacron/30% wool knit, (2) a tan shade on 100% textured polyester woven fabric, and (3) a brown shade on a 100% textured polyester woven fabric. Separate dyeings were run with plant water, and both 75% and 90% recovery product water from both the Selas and UOP modules. All dyeings were run on a high-temperature pressurized beaker bath laboratory machine in 250 mℓ beakers at a fabric-to-liquor ratio of 14:1.

No problems were encountered with the use of the product water for laboratory test dyeings and the fastness properties of the dyed fabric were the same as those obtained with normal plant water.

Reuse of Concentrate

The concentrates from 75% and 90% recoveries were evaluated in laboratory tests for a package dye system. The staining caused by the chemicals and dyes present in the concentrate made the fabric unsuitable for commercial use. No value could be observed from reuse of the concentrate obtained from the composite waste stream.

It is possible, when the wastewater and chemicals are recovered by hyperfiltration, to change the process to (1) achieve faster dyeing cycles, and/or (2) to eliminate the need for some auxiliary chemicals. For example, with direct dyeing of cellulose, salt can be eliminated by using higher concentrations of dye in the dyebath. Excess dyestuffs will be recovered by the membranes for reuse in the next cycle. Depending on the amount of fiber dyed and range of colors, this modification may or may not be practical. Water, chemicals, and energy requirements will play a major role in the selection of dyeing processes used in the future.

MEMBRANE PERFORMANCE

The UOP cellulose acetate and the dynamic membranes were operated on pretreated composite wastewater (Table H-2) for 200 hours beginning on July 16, 1975. The performance of the membranes was monitored by periodic measurements of the product water flow rate through the membranes and the conductivity rejection.

The UOP cellulose acetate and the dynamic Zr-PAA membranes were fed from a common tank. The incoming feed was neutralized to pH ≈ 7 - 9.5 with sulfuric acid and controlled in that range. Table H-5 shows analyses performed on feed water after neutralization and 25-micron filtration. The volumetric recovery was allowed to rise to ∿90%, and was maintained there

TABLE H-5. CHEMICAL ANALYSES OF WASTEWATER TREATED[a] FOR MEMBRANE PERFORMANCE TESTS AT PLANT #82

SAMPLE NUMBER	800	816
DATE TAKEN	7/16/75	7/25/75
PARAMETER[b]		
COD	717	310
BOD	144	59
TOC	510	210
Alkalinity	77	91
Hardness	12	8
Total Solids	2515	928
Dissolved Solids	2364	736
Volatile Solids	423	323
Color	170	120
Turbidity	50	40
Conductivity	3100	1100
Phenol	0.04	0.045
pH	6.3	7.0
Mercury	-	-
Manganese	0.07	0.07
Calcium	1.90	2.16
Iron	0.89	0.97
Nickel	0.20	0.20
Chromium	0.10	0.10
Zinc	0.28	0.91
Copper	0.25	0.29
Magnesium	1.27	0.89

[a] Grab samples of total plant effluent with 25-micron prefiltration, followed by neutralization to pH ∿ 6.5.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

throughout the remainder of the 200-hour test. The temperature was maintained at near 30°C, the average temperature of the plant outfall.

Dynamic Membrane

Three modules of Selas ceramic tubes with dynamic Zr-PAA membranes were evaluated. The performance is summarized in Figure H-2, a plot of flux and rejection throughout the test period. One of the modules, #19, was equipped with new membranes and therefore had a somewhat higher initial flux. Module #4 was equipped with eighteen-month old membranes that had already been used at several other plants. This older membrane exhibited a lower initial flux.

The effect of fluid velocity on flux decline was the subject of parametric testing. No significant effects of velocity variation were observed. The flux of 1.0 m/d (25 gallons/ft^2/d) at 31°C and 6.9 MPa (1000 psig) is used in design cost projections.

The conductivity rejection allows measurement of the electrolyte filtration by the membrane. The filtration efficiency for larger organic molecules is usually higher than for the electrolytes. Grab samples of the concentrate and product waters passing through the membranes were obtained during the 200-hour performance tests and analyzed to indicate the filtration efficiency for several constituents. The results of analyses for three pairs of samples are shown in Tables H-6 through H-8.

The high rejections of organics, indicated by COD, BOD, and color comparisons between the concentrate and product samples are greater than the conductivity rejections. The rejection of metals is very high, as indicated in cases where results are significantly above the limit of detection.

Cellulose Acetate Membrane

The performance of the UOP spiral-wound cellulose acetate module is summarized in Figure H-3, a plot of flux and rejection throughout the test period. The operating conditions were: 2.1 - 2.6 MPa (300 - 320 psig) and feed rate of 9.8 - 13 dm^3/min (2.6 - 3.5 gallons per minute). The module evaluated had not been previously exposed to wastewater.

The flux declined during the first 50 hours of the test. No washing procedures were attempted, but the flux achieved a stable value at about 0.2 m/d. The conductivity rejection was in the range of 90 - 95% throughout the 200-hour test period. The rejection of other constituents was very high, as indicated by the analyses results in Tables H-6 through H-8.

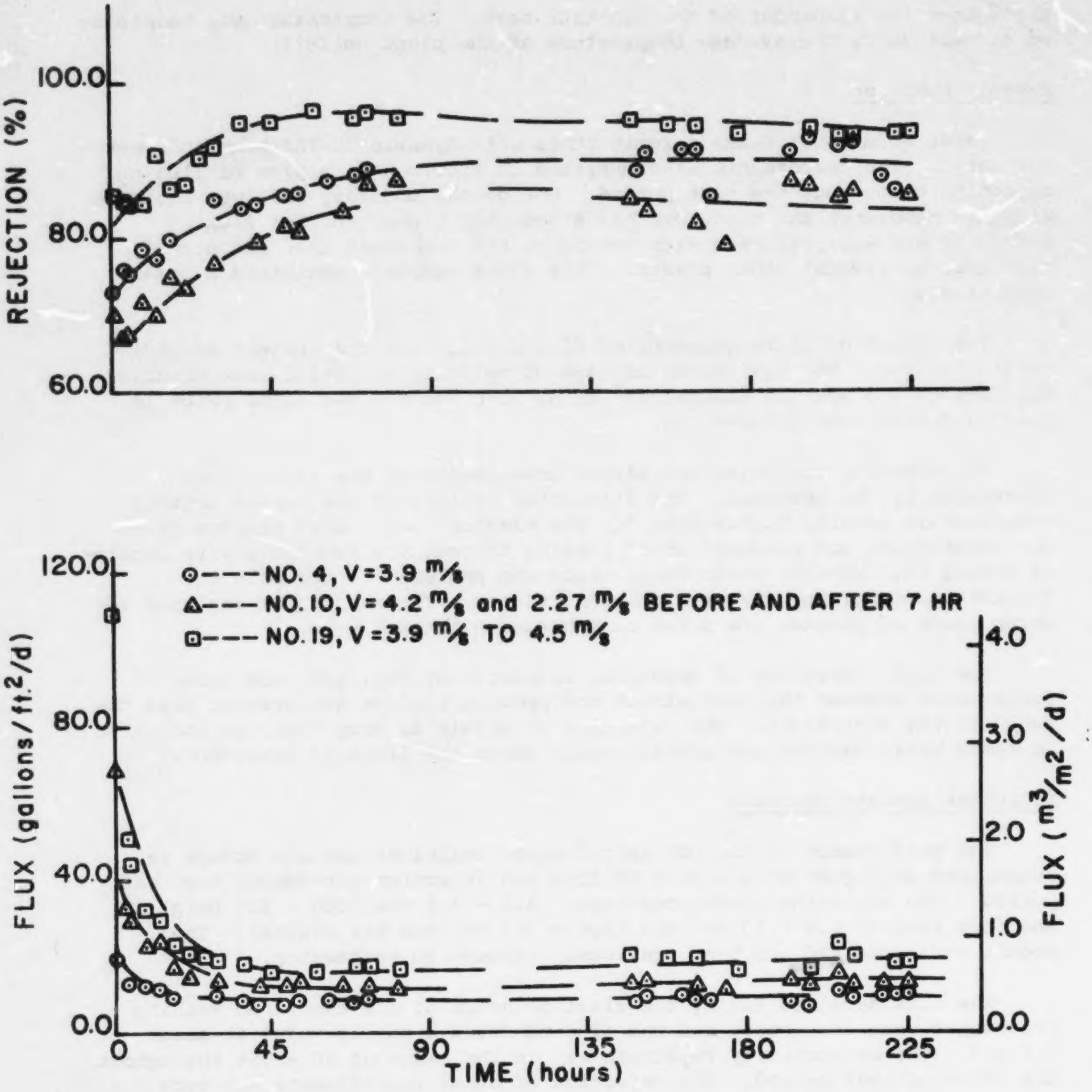

Figure H-2. Hyperfiltration of combined effluent at Plant #82 by Zr(IV)-PAA membranes on Selas ceramic supports. (P = 6.9 MPa (1000 psig); T = 31°C; pH = 4.7 - 9.9; recovery = 90%.)

TABLE H-6. PERFORMANCE PARAMETERS OF SELAS AND UOP MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #82

TYPE	Selas[a] Product	Selas/UOP Concentrate	UOP[b] Product
SAMPLE NUMBER	802	803	804
DATE TAKEN	7/17/75	7/17/75	7/17/75
PARAMETER[c]			
COD	224	3500	131
BOD	28	460	38
TOC	70	1300	70
Alkalinity	59	62	5
Hardness	4	112	2
Total Solids	1459	10937	182
Dissolved Solids	1476	10354	86
Volatile Solids	81	1717	105
Color	15	660	2
Turbidity	20	210	2
Conductivity	2500	13000	110
Phenol	0.08	0.11	0.10
pH	6.1	5.2	5.1
Mercury	-	-	-
Manganese	0.07	0.29	0.07
Calcium	0.96	27.3	0.56
Iron	0.10	8.25	0.10
Nickel	0.20	1.02	0.20
Chromium	0.10	0.20	0.10
Zinc	0.43	12.6	0.05
Copper	0.25	3.07	0.25
Magnesium	0.32	8.40	0.02

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] UOP module contained spiral-wound cellulose acetate membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE H-7. PERFORMANCE PARAMETERS OF SELAS AND UOP MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #82

TYPE	Selas[a] Product	Selas/UOP Concentrate	UOP[b] Product
SAMPLE NUMBER	811	812	813
DATE TAKEN	7/22/75	7/22/75	7/22/75
PARAMETER[c]			
COD	69	1900	36
BOD	8	140	1
TOC	12	720	18
Alkalinity	64	274	7
Hardness	2	103	2
Total Solids	597	8251	182
Dissolved Solids	546	7658	42
Volatile Solids	398	1407	159
Color	0	700	0
Turbidity	0	60	0
Conductivity	980	10200	49
Phenol	0.005	0.10	0.08
pH	6.8	6.8	6.1
Mercury	-	-	-
Manganese	0.07	0.33	0.07
Calcium	0.63	27.1	0.37
Iron	0.10	8.89	0.10
Nickel	0.20	1.20	0.20
Chromium	0.10	0.57	0.10
Zinc	0.08	3.89	0.02
Copper	0.25	1.18	0.25
Magnesium	0.08	7.29	0.01

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] UOP module contained spiral-wound cellulose acetate membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE H-8. PERFORMANCE PARAMETERS OF SELAS AND UOP MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #82

TYPE	Selas[a] Product	Selas/UOP Concentrate	UOP[b] Product
SAMPLE NUMBER	817	818	819
DATE TAKEN	7/25/75	7/25/75	7/25/75
PARAMETER[c]			
COD	61	775	49
BOD	2	27	3
TOC	20	290	50
Alkalinity	53	21	10
Hardness	2	49	2
Total Solids	241	4002	15
Dissolved Solids	240	4002	14
Volatile Solids	142	842	10
Color	3	400	0
Turbidity	0	30	0
Conductivity	550	5100	32
Phenol	0.025	0.05	0.025
pH	7.1	7.2	6.6
Mercury	-	-	-
Manganese	0.07	0.18	0.07
Calcium	0.49	16.2	0.41
Iron	0.10	3.16	0.10
Nickel	0.20	0.63	0.20
Chromium	0.10	0.20	0.10
Zinc	0.05	3.02	0.02
Copper	0.25	0.74	0.25
Magnesium	0.04	3.67	0.02

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] UOP module contained spiral-wound cellulose acetate membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

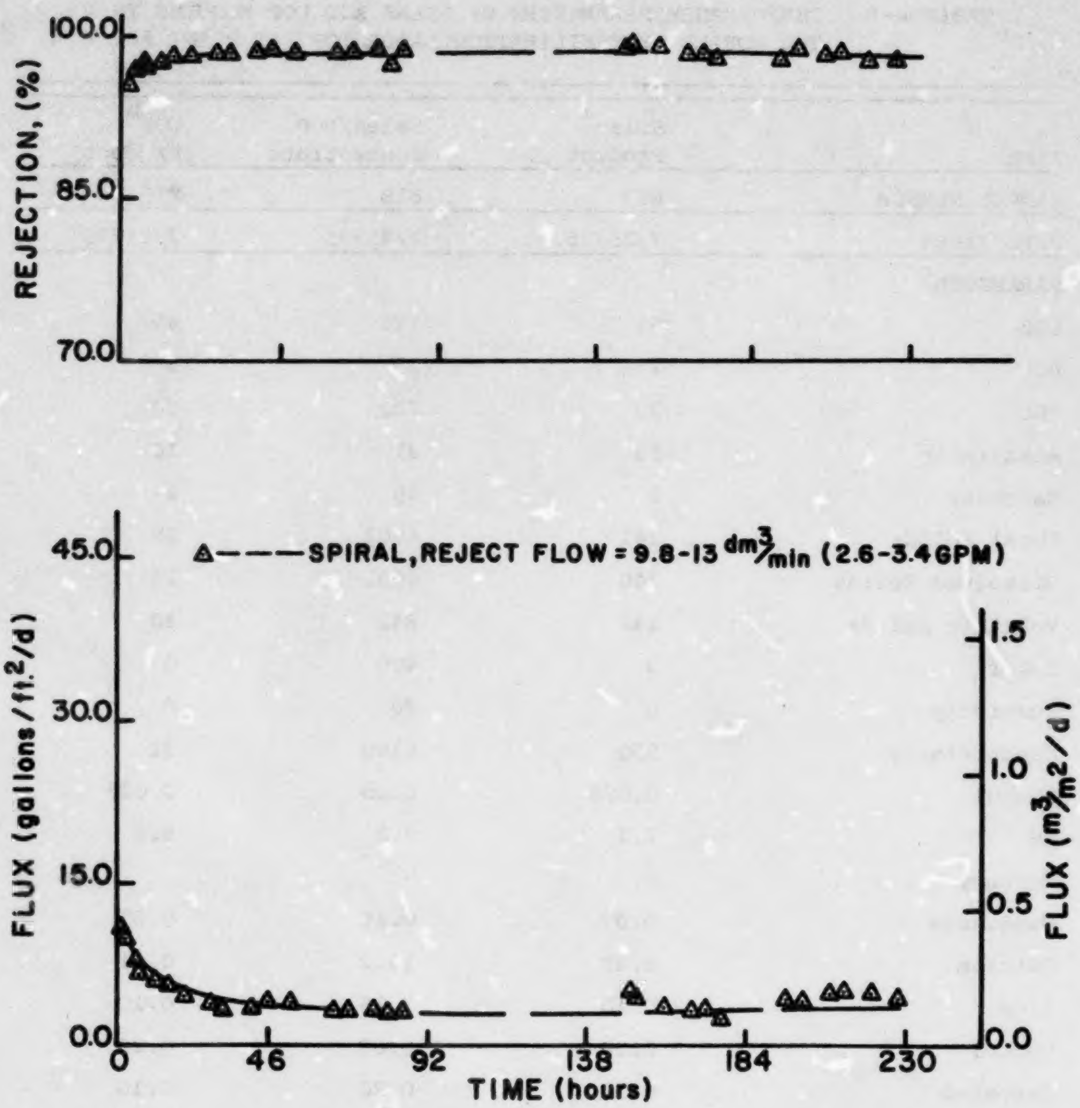

Figure H-3. Hyperfiltration of combined effluent at Plant #82 by a UOP spiral-wound module with cellulose acetate membranes. (P = 2.1 - 2.59 MPa (300 - 370 psig); T = 30°C; pH = 4.7 - 9.7; recovery = 90%.)

APPENDIX I

PLANT #83

The on-site tests conducted from July 30, 1975, to September 4, 1975, were to obtain the following information: (1) plant laboratory evaluation of reuse, and (2) engineering performance data with membranes. Reuse of both the purified product water and the concentrated residue was evaluated in laboratory tests conducted by Plant #83 personnel. Samples of wastewater, purified product water, and concentrated residue were analyzed by Nardin Laboratory.[a] In addition, the treatability of the concentrated residue was evaluated in bench-scale tests, Appendix J.

The production parameters of Plant #83, Table I-1, provide a basis for evaluation of the results of the project. The factors are important in the evaluation of the practicality of scale-up from the pilot plant.

FIBERS AND CHEMICALS

The primary processes at Plant #83 are scouring, bleaching, dyeing, and finishing of cotton and cotton/polyester blended fabrics on continuous ranges. The dyes used in the plant are those common to the finishing of cotton and polyester fibers: sulfur, vat, fiber reactive, disperse, and napthol dyes.

Ninety percent of the 32,197 m^3/d (8,500,000 gallons/day) total water usage is in wet finishing. Allowing for evaporation in the dyehouse, the composite waste stream is at least 30% by volume dyehouse wastewater.

WASTEWATER CHARACTERISTICS

The variety of dyes and scouring chemicals used produce a complex and variable waste stream composition. The wastewater characteristics, based on a monthly average for the summer of 1975, of plant wastewater discharge parameters are: BOD_5 = 400 mg/ℓ; COD = 1580 mg/ℓ; total suspended solids = 170 mg/ℓ; total dissolved solids = 1950 mg/ℓ; pH = 10.3; temperature = 90°F. Tables I-2, I-3, and I-4 present the results of analyses for six grab samples

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[a] Division of Commonwealth Laboratory, Inc., Greenville, SC.

TABLE I-1. PLANT #83 PRODUCTION CAPACITY PARAMETERS

QUANTITIES USED	
Materials: cotton, cotton/polyester	
Water (total to plant), m^3/day	32,197
(gallons/day)	(8,500,000)
Water (to dyehouse), m^3/day	9,659
(gallons/day)	(2,550,000)
Dyes, kg/day	5,293
(pounds/day)	(11,644)
Auxiliary Chemicals, kg/day	21,130
(pounds/day)	(46,486)
Energy (for process steam), joules/day	8490×10^9
(Btu/day)	(8087×10^6)
UNIT COSTS	
Water, ¢/m^3	3
(\$/1000 gallons)	(6.12)
Fuel, ¢/10^7 joules	1.4
(\$/10^6 Btu)	(1.51)

TABLE I-2. CHEMICAL ANALYSES OF PLANT #83 WASTEWATER[a]

SAMPLE NUMBER	829	832	838
DATE TAKEN	8/6/75	8/8/75	8/11/75
PARAMETER[b]			
COD	1312	1689	2784
BOD	404	340	480
TOC	425	330	-
Alkalinity	510	657	382
Hardness	26	26	-
Total Solids	1800	1640	1612
Dissolved Solids	1783	1560	1396
Volatile Solids	1204	1020	1108
Color	-	-	-
Turbidity	80	187	89
Conductivity	1650	2000	-
Phenol	17	58	-
pH	11.15	11.25	10.70
Mercury	-	-	-
Manganese	0.01	0.01	-
Calcium	2.4	0.38	-
Iron	0.09	0.58	-
Nickel	0.3	0.19	-
Chromium	0.02	0.1	-
Zinc	1.9	0.55	-
Copper	3.4	0.6	-
Magnesium	6.0	3.5	-

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE I-3. CHEMICAL ANALYSES OF PLANT #83 WASTEWATER[a]

SAMPLE NUMBER	840	843
DATE TAKEN	8/12/75	8/13/75
PARAMETER[b]		
COD	2112	-
BOD	513	-
TOC	-	-
Alkalinity	626	-
Hardness	-	-
Total Solids	1172	-
Dissolved Solids	712	-
Volatile Solids	920	-
Color	-	-
Turbidity	140	-
Conductivity	-	-
Phenol	-	-
pH	10.70	-
Mercury	-	-
Manganese	-	-
Calcium	-	-
Iron	-	-
Nickel	-	-
Chromium	-	-
Zinc	-	-
Copper	-	-
Magnesium	-	-

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE I-4. CHEMICAL ANALYSES OF PLANT #83 WASTEWATER[a]

SAMPLE NUMBER	848	852
DATE TAKEN	8/14/75	8/15/75
PARAMETER[b]		
COD	1248	1344
BOD	393	413
TOC	312	315
Alkalinity	286	427
Hardness	26	26
Total Solids	1392	2340
Dissolved Solids	1192	2196
Volatile Solids	928	1320
Color	-	-
Turbidity	58	67
Conductivity	1200	2700
Phenol	22	85
pH	10.70	11.15
Mercury	-	-
Manganese	0.60	0.1
Calcium	1.6	1.5
Iron	0.2	0.3
Nickel	0.02	0.48
Chromium	0.05	0.02
Zinc	2.7	0.1
Copper	0.4	0.4
Magnesium	5.0	40

[a] Grab samples of total plant effluent.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

obtained during the period of on-site testing. Plant #83 is classified as Subcategory 8, commissioned finishing.[a]

SCHEDULE AND PROCEDURE

Schedule

Testing was begun on August 5, 1975. Initially, one-gallon (3.8ℓ) samples of purified product and concentrate were collected for reuse evaluation in the plant laboratory. The UOP[b] module was then taken out of operation for the remainder of Plant #83's testing program. A 38ℓ sample of concentrate was later collected for the biological treatability study.

The following is a summary of events at Plant #83:

07/30 - Arrived from Plant #82; utilities connected.

08/05 - Began parametric performance test with UOP and Selas[c] modules.

08/07 - Reuse test samples generated.

08/13 - Use of UOP module discontinued.

08/15 - Parametric performance test completed.

08/21 - Began special tests utilizing Selas and Union Carbide[d] modules.

08/28 - Special tests completed.

09/04 - Returned to Clemson University.

Procedure

The membranes for evaluation were selected based on availability and the characteristics of the wastewater. The wastewater was prefiltered through 25-micron cartridge filters prior to entering the mobile laboratory. The pH was adjusted when necessary to meet membrane manufacturer specifications. Figure I-1 shows schematically the equipment arrangement. Three types of membranes were employed in these tests: the UOP spiral-wound cellulose acetate membrane, the dual-layer dynamic membrane on the Selas ceramic tubes, and the Union Carbide tubular ultrafilter.

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[a] Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Textile Point Source Category. EPA-440/1-74-022-a, US Environmental Protection Agency, Washington, DC, 1974.

[b] Universal Oil Products, ROGA Division.

[c] Selas Corporation of America, Flotronics Division.

[d] Union Carbide.

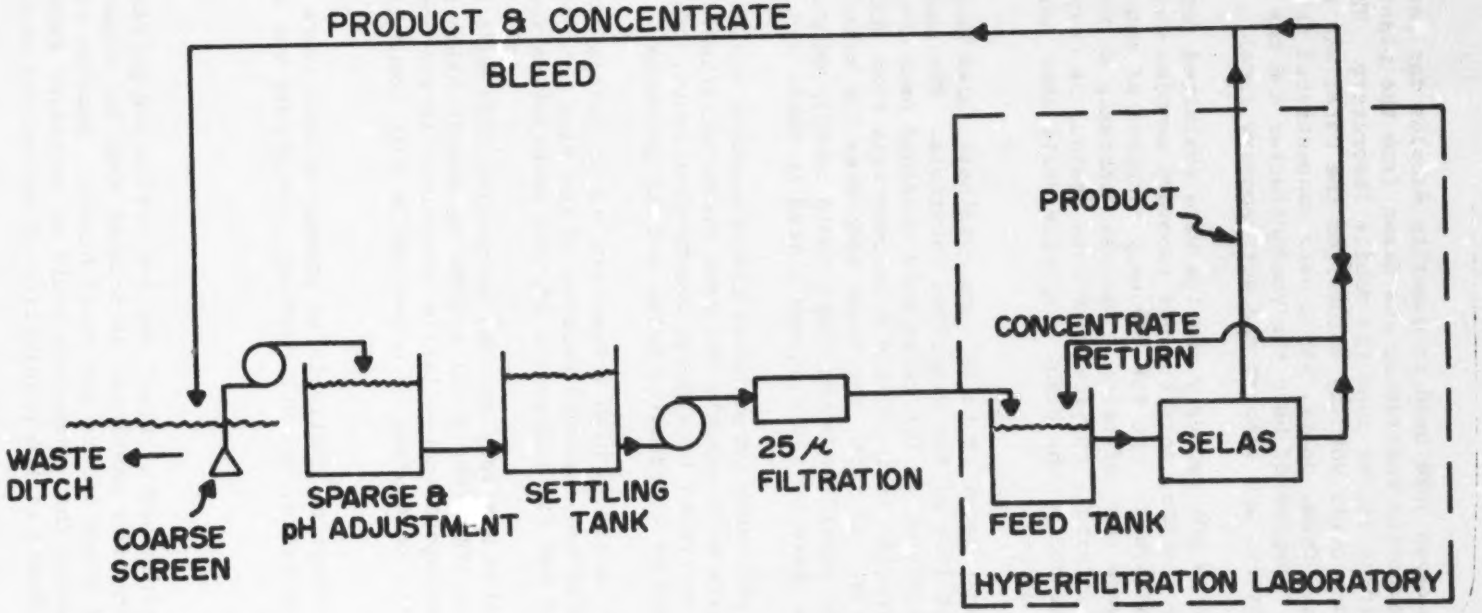
PRODUCT & CONCENTRATE
BLEED
PRODUCT
CONCENTRATE
RETURN
WASTE
DITCH
COARSE
SCREEN
SPARGE &
pH ADJUSTMENT
SETTLING
TANK
25 μ
FILTRATION
FEED TANK
SELAS
HYPERFILTRATION LABORATORY

Figure I-1. Flow schematic for equipment set-up at Plant #83.

REUSE

All types of membranes were used to generate samples for reuse evaluation. A sample of composite wastewater was drawn from the plant sewer, and pumped through a 25-micron filter into the mobile laboratory. The hyperfiltration was conducted until 90% (by volume) of the water was recovered as purified product water. Dyes, salts, etc., were concentrated in the remaining 10% of the water. Samples of both the product water and the concentrate were taken at 75% recovery, and also at the 90% recovery level.

Both the 75% and the 90% recovery samples were evaluated for reuse. However, for budgetary reasons, only the 90% recovery samples were subjected to detailed chemical analyses. The 90% recovery samples, of course, represent the more severe test of reuse. Because membranes do not separate 100% of the dissolved material, the 10% by volume residue is only about eight times as concentrated as the plant composite wastewater (instead of the volumetric factor of ten).

The purified product water contains some chemicals, also because the membranes do not reject 100% of the dissolved materials. The samples of purified product water evaluated for reuse were obtained near the end of the concentration (90%), and thus contain more chemicals than the average product water would have. In fact, for these membranes the mixed product water from a full-scale hyperfiltration plant would contain only about one-third the contaminants shown by the analyses listed in Table I-5.

The two types of membranes were tested simultaneously and therefore processed composite waste with exactly the same characteristics. The collection of samples for reuse took about twenty-four hours. The concentration was accomplished by withdrawing Selas and UOP products.

The product water contained high concentrations of solids (885 mg/ℓ) and COD (103 mg/ℓ). This was expected because of the high concentrations in the waste stream and was not indicative of poor membrane performance.

The concentrate water was very strong, containing 7030 mg/ℓ total solids, and 2700 mg/ℓ of COD. The total solids are mostly salts as indicated by the high (75%) percentage of non-volatile substances in the concentrate. This data agrees with the percentage of non-volatile salt found in the plant effluent.

Since it may not always be desirable to attempt direct reuse or reclamation of the concentrate, the 90% recovery concentrate was used in the treatability tests.

REUSE EVALUATION

Since the fibers processed by Plant #83 are cotton and polyester, the waste stream contains the many chemicals associated with the scouring, desizing, and dyeing of these fibers and their blends. Because of this there was little likelyhood that chemicals could be recovered from the concentrated residue. There is the possibility of recovering chemicals

TABLE I-5. CHEMICAL ANALYSES OF WATER EVALUATED FOR REUSE[a] AT PLANT #83

(90% Water Recovery)

TYPE	UOP/Selas Concentrate	UOP[b] Product	Selas[c] Product
SAMPLE NUMBER	824	826	828
DATE TAKEN	8/6/75	8/6/75	8/6/75
PARAMETER[d]			
COD	2700	53	103
BOD	210	11	8
TOC	2000	43	39
Alkalinity	220	200	64
Hardness	220	10	10
Total Solids	7030	74	886
Dissolved Solids	6987	74	885
Volatile Solids	1770	48	76
Color	1400	10	15
Turbidity	770	0.5	1.0
Conductivity	6800	83	1550
Phenol	0.08	0.14	0.015
pH	7.0	6.0	6.8
Mercury	<0.001	<0.001	<0.001
Manganese	<0.01	<0.01	<0.09
Calcium	1.62	0.73	0.51
Iron	0.98	<0.01	<0.01
Nickel	<0.01	<0.01	<0.01
Chromium	0.07	<0.01	<0.01
Zinc	0.39	0.16	0.71
Copper	<0.01	0.05	0.09
Magnesium	10.5	0.62	0.71

[a] Reuse tests conducted in Plant #83 dye laboratory.

[b] UOP module contained spiral-wound cellulose acetate membranes.

[c] Selas module contained ceramic tubes with dynamic membranes.

[d] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

from isolated process waste streams. The analyses results for the purified product water and the concentrated residue from both the cellulose acetate and the dynamic membranes are presented in Table I-5.

Reuse of Product Water

As a stringent test of the reuse of the product water, the 90% recovery samples were evaluated. The analyses of the product water indicates that, in general, the COD and dissolved solids are much more than expected for tap water.

All of the purified product water generated by the mobile laboratory at Plant #83 was evaluated in the plant laboratory and found suitable for reuse in the plant.

The product water was used in the laboratory to dye 55/45 polyester avril fabric, 100% T-64 polyester fabric, and 100% orlon and multifiber test cloth. The procedures employed in the test dyeings were standard for continuous dyeing. All of the purified product water was found suitable for general reuse as dyehouse process water. No problems were encountered with color-fastness or any other property.

Reuse of Concentrate

The concentrate water from 70% and 95% water recoveries were evaluated for process water using exactly the same procedures and chemicals as used with the product water reuse tests. No reuse value was determined for the concentrate.

It is possible, when the wastewater and chemicals are recovered by hyperfiltration, to change the process to (1) achieve faster dyeing cycles, and/or (2) to eliminate the need for some auxiliary chemicals. For example, with direct dyeing of cellulose, salt can be eliminated by using higher concentrations of dye in the dyebath. Excess dyestuffs will be recovered by the membranes for reuse in the next cycle. Depending on the amount of fiber dyed and range of colors, this modification may or may not be practical. Water, chemicals, and energy requirements will play a major role in the selection of dyeing processes used in the future.

MEMBRANE PERFORMANCE

The cellulose acetate and dynamic membrane were operated on pretreated composite wastewater (Table I-2) for 87 and 200 hours, respectively, beginning on August 8, 1975. The performance of the membranes was monitored by periodic measurements of the product water flow rate through the membranes and the conductivity rejection.

The membranes were fed from a common tank. The incoming feed was neutralized to pH ≈ 7 with sulfuric acid and controlled at that level. Tables I-6 and I-7 show analyses performed on feed water after neutralization and 25-micron filtration. The volumetric recovery was allowed to rise to ~90%, to obtain samples for reuse evaluation, and was maintained there

TABLE I-6. CHEMICAL ANALYSES OF WASTEWATER TREATED[a] FOR MEMBRANE PERFORMANCE TESTS AT PLANT #83

SAMPLE NUMBER	830	835
DATE TAKEN	8/6/75	8/8/75
PARAMETER[b]		
COD	1216	-
BOD	335	-
TOC	267	-
Alkalinity	151	-
Hardness	36	-
Total Solids	1984	-
Dissolved Solids	1844	-
Volatile Solids	884	-
Color	-	-
Turbidity	115	-
Conductivity	1700	-
Phenol	126	-
pH	6.40	-
Mercury	-	-
Manganese	0.08	-
Calcium	2.4	-
Iron	7.9	-
Nickel	0.09	-
Chromium	0.5	-
Zinc	0.7	-
Copper	0.6	-
Magnesium	6.3	-

[a] Grab samples of combined plant effluent with 25-micron prefiltration, followed by neutralization to pH ∿ 6.5.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE I-7. CHEMICAL ANALYSES OF WASTEWATER TREATED[a] FOR MEMBRANE PERFORMANCE TESTS AT PLANT #83

SAMPLE NUMBER	839	849
DATE TAKEN	8/11/75	8/14/75
PARAMETER[b]		
COD	1632	960
BOD	360	367
TOC	-	295
Alkalinity	0	166
Hardness	-	52
Total Solids	2096	1720
Dissolved Solids	1920	1634
Volatile Solids	808	788
Color	-	-
Turbidity	145	176
Conductivity	-	1700
Phenol	-	480
pH	3.95	9.25
Mercury	-	-
Manganese	-	0.1
Calcium	-	1.8
Iron	-	6.7
Nickel	-	0.17
Chromium	-	0.4
Zinc	-	0.8
Copper	-	1.15
Magnesium	-	4.5

[a] Grab samples of combined plant effluent with 25-micron prefiltration, followed by neutralization to pH ∿ 6.5.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

throughout the remainder of the 200-hour test. The temperature was maintained at near 35°C while the UOP module was in use and at 55°C after it was removed. The UOP module was removed from service twice for cleaning. At 148 hours, a settling barrel was placed in the feed between the pH adjustment site and the 25-micron filters. This alleviated the rapid fouling of the UOP spiral-wound module.

Dynamic Membrane

Three modules of Selas ceramic tubes with dynamic Zr-PAA membranes were evaluated. The performance is summarized in Figure I-2, a plot of flux and rejection throughout the test period. One of the modules, #14, was equipped with new membranes and therefore had a somewhat higher initial flux. Module #4 was equipped with fifteen-month old membranes that had already been used at several other plants. This older membrane exhibited a lower initial flux.

The effect of fluid velocity on flux decline was the subject of parametric testing. At 148 hours, the velocity for Module #10 was reduced from 4.5 m/s (15 fps) to 3.3 m/s (10 fps). This change in velocity had no discernable effect on the flux decline. The flux used in the design cost projections is 0.5 m/d (13 gallons/ft^2/d) at 37°C and 6.9 MPa (1000 psig).

The conductivity rejection allows measurement of the electrolyte filtration by the membrane. The filtration efficiency for larger organic molecules is usually higher than for the electrolytes. Grab samples of the concentrate and product waters passing through the membranes were obtained during the 200-hour performance tests and analyzed to indicate the filtration efficiency for several constituents. The results of analyses for three pairs of samples are shown in Tables I-8 through I-11.

The high rejections of organics, indicated by COD, BOD, and color comparisons between the concentrate and product samples are greater than the conductivity rejections. The phenol rejection is about 88%. The rejection of metals is very high, as indicated in cases where results are significantly above the limit of detection.

Cellulose Acetate Membrane

The performance of the cellulose acetate membrane module is summarized in Figure I-3, a plot of flux and rejection throughout the test period. The operating conditions were specified by the manufacturer: 2.4 MPa (350 psig) and a feed rate of 0.8 - 0.9 m^3/hr (3.5 - 4 gallons per minute). The module tested had been used at previous test sites. The module had to be cleaned twice due to the accumulation of particulates. Flux was severely effected but rejections remained high throughout the test. It is assumed that better prefiltration than was available with the mobile laboratory would solve the problem. The results of two pairs of samples of product and concentrate are shown in Tables I-10 and I-12.

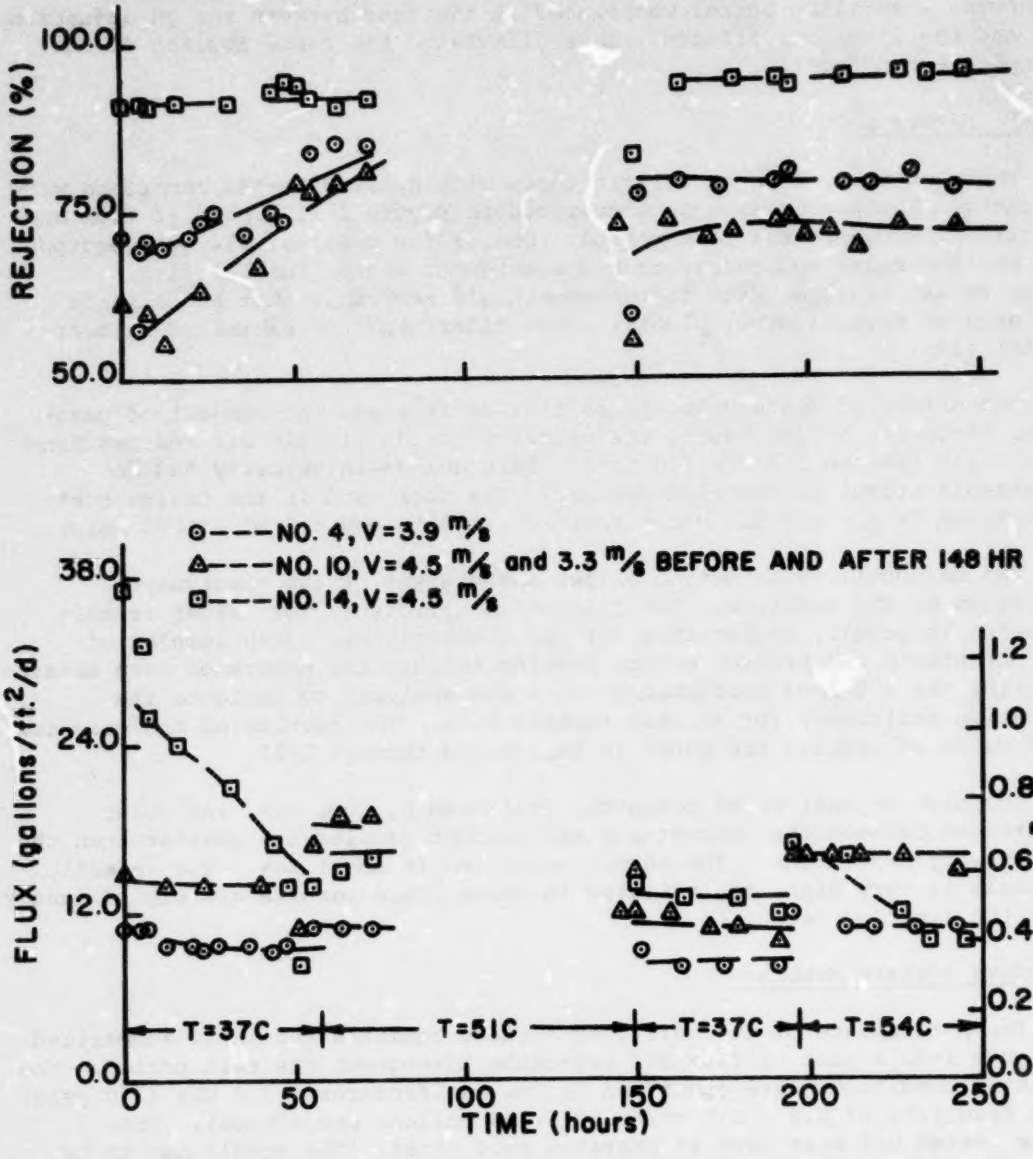

Figure I-2. Hyperfiltration of combined effluent at Plant #83 by Zr(IV)-PAA membranes on Selas ceramic supports. (P = 6.31 MPa (920 psig); pH = 4.0 - 9.8; recovery = 90%.)

TABLE I-8. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #83

SAMPLE NUMBER	833	834
TYPE	Product	Concentrate
DATE TAKEN	8/8/75	8/8/75
PARAMETER[b]		
COD	105	3696
BOD	23	310
TOC	8	620
Alkalinity	107	507
Hardness	1	260
Total Solids	468	5160
Dissolved Solids	468	5080
Volatile Solids	324	1752
Color	-	-
Turbidity	3	74
Conductivity	1000	4700
Phenol	5	157.5
pH	9.90	9.60
Mercury	-	-
Manganese	0.01	0.15
Calcium	0.003	5.9
Iron	0.02	13
Nickel	0.02	0.80
Chromium	0.02	0.7
Zinc	0.005	1.2
Copper	0.01	0.8
Magnesium	0.1	25

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[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE I-9. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #83

SAMPLE NUMBER	836	837
TYPE	Product	Concentrate
DATE TAKEN	8/11/75	8/11/75
PARAMETER[b]		
COD	40	2900
BOD	50	533
TOC	16	760
Alkalinity	248	353
Hardness	2	117
Total Solids	488	5800
Dissolved Solids	488	5715
Volatile Solids	196	2256
Color	-	-
Turbidity	2	71
Conductivity	880	5200
Phenol	10	315
pH	9.95	9.35
Mercury	-	-
Manganese	0.01	0.15
Calcium	0.003	4.05
Iron	0.02	20
Nickel	0.02	1.04
Chromium	0.02	0.7
Zinc	0.005	1.65
Copper	0.01	2.2
Magnesium	28	28

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE I-10. PERFORMANCE PARAMETERS OF SELAS AND UOP MODULES IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #83

TYPE	Selas/UOP Concentrate	Selas[a] Product	UOP[b] Product
SAMPLE NUMBER	845	846	847
DATE TAKEN	8/13/75	8/13/75	8/13/75
PARAMETER[c]			
COD	500	20	30
BOD	143	8	9
TOC	232	7	9
Alkalinity	128	65	26
Hardness	221	6	1
Total Solids	3176	396	84
Dissolved Solids	3138	396	84
Volatile Solids	576	176	84
Color	-	-	-
Turbidity	47	2.5	2.6
Conductivity	4000	780	100
Phenol	35	5	5
pH	6.80	7.20	6.90
Mercury	-	-	-
Manganese	0.15	0.01	0.01
Calcium	6.15	0.2	0.003
Iron	12.0	0.02	0.02
Nickel	0.48	0.02	0.02
Chromium	0.4	0.02	0.02
Zinc	0.1	0.005	0.005
Copper	0.2	0.01	0.01
Magnesium	14	0.355	0.0005

[a] Selas module contained ceramic tubes with dynamic membranes.

[b] UOP module contained spiral-wound cellulose acetate membranes.

[c] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

TABLE I-11. PERFORMANCE PARAMETERS OF SELAS MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #83

SAMPLE NUMBER	850	851
TYPE	Product	Concentrate
DATE TAKEN	8/15/75	8/15/75
PARAMETER[b]		
COD	57	2304
BOD	16	323
TOC	12	750
Alkalinity	121	578
Hardness	5	221
Total Solids	480	4840
Dissolved Solids	480	4720
Volatile Solids	244	1992
Color	-	-
Turbidity	4.1	83
Conductivity	900	3500
Phenol	375	310
pH	7.65	7.55
Mercury	-	-
Manganese	0.01	0.2
Calcium	0.07	4.5
Iron	0.02	20
Nickel	0.02	0.90
Chromium	0.02	1
Zinc	0.005	2.15
Copper	0.01	1.6
Magnesium	20	31.5

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[a] Selas module contained ceramic tubes with dynamic membranes.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

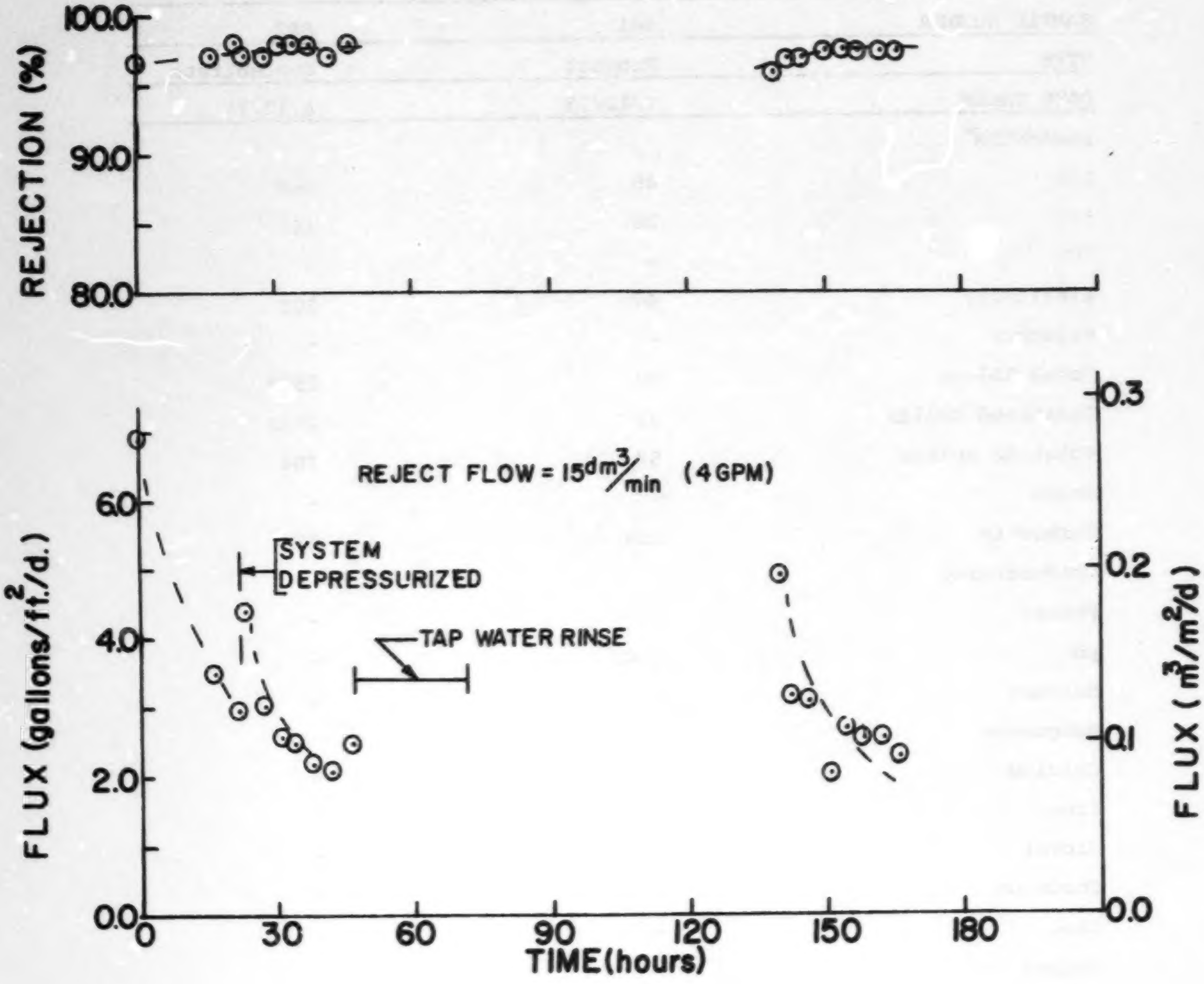

Figure I-3. Hyperfiltration of combined effluent at Plant #83 by cellulose acetate membranes in a UOP spiral-wound module.

TABLE I-12. PERFORMANCE PARAMETERS OF UOP MODULES[a] IN THE MOBILE HYPERFILTRATION LABORATORY AT PLANT #83

SAMPLE NUMBER	841	842
TYPE	Product	Concentrate
DATE TAKEN	8/12/75	8/12/75
PARAMETER[b]		
COD	48	768
BOD	16	147
TOC	-	-
Alkalinity	44	103
Hardness	-	-
Total Solids	52	2588
Dissolved Solids	52	2532
Volatile Solids	52	784
Color	-	-
Turbidity	2.9	52
Conductivity	-	-
Phenol	-	-
pH	6.05	-
Mercury	-	-
Manganese	-	-
Calcium	-	-
Iron	-	-
Nickel	-	-
Chromium	-	-
Zinc	-	-
Copper	-	-
Magnesium	-	-

[a] UOP module contained spiral-wound cellulose acetate membranes.

[b] All results are in mg/ℓ, except for color (Pt-Co units), turbidity (FTU), conductivity (μmho/cm), and pH (unitless).

APPENDIX J

BIOLOGICAL AND CHEMICAL TREATABILITY OF HYPERFILTRATION CONCENTRATE

As the technological capabilities of hyperfiltration (reverse osmosis) for the treatment of textile wastes increase, it has become necessary to examine the feasibility of chemical and/or biological treatment of the concentrated wastewater left behind after product water has been recovered for recycle to the plant.

This appendix is a summary of the study conducted for the South Carolina Textile Manufacturers Association (SCTMA) to determine the biological and chemical treatability of textile waste concentrates. A more detailed report is on file at the SCTMA offices in Columbia, South Carolina. The concentrates were obtained from six of the eight textile plants where the mobile hyperfiltration laboratory was operated.

HYPERFILTRATION

The membranes utilized in the mobile laboratory were manufactured by Selas, Universal Oil Products, and Westinghouse (now Union Carbide). The concentrate wastewater examined in this study represent six different textile plants conducting most of the wet finishing operations found in the textile industry. The pH range of the raw plant wastewater ranged from 4 to 11. The operating temperatures ranged from 30°C to 65°C depending on the process characteristics and hyperfiltration membrane being used. The wastewater was pretreated by 25-micron prefiltration with cartridge filters and the pH was adjusted as necessary for the specific membrane system being used.

Membranes effect a separation of the wastewater into a product stream which is the concentrated residue of impurities after removal of the product stream. In the systems as operated for these tests, the concentrate was returned to the raw wastewater holding tank and was thereby recycled through the system a number of times. The membrane systems utilized in these tests were operated to achieve from 80 to 92% recovery of product water; that is, the recycling process was continued until 80 to 92% of the original volume of wastewater was recovered as clean product water. As a result, the impurities remained in the 8 to 20% volume of concentrate. The concentrate was used in this study for biological and chemical treatment.

The characteristics of the membrane concentrates for all six plants are given in Table J-1. The characteristics of the raw wastewater feed to

TABLE J-1. CONCENTRATE WASTE CHARACTERIZATION

Non-metal Analyses[a]	#60	#70	#40	#80	#81	#82
COD	2500	3720	15285	4032	8871	2496
Filtered COD					7942	2487
TOC	935	1410	5753	707	4140	1606
BOD_5	270	1078	1547	561	3745	860
BOD_{10}	415	1600	2200	300	4700	925
BOD_{15}	515	1800	3500	475	4450	1175
BOD_{20}	560	1600	4500	700	4700	1100
BOD_{30}	820	2200	5000	425	3000	450
Solids						
Total	3760	5028	10028	9870	8702	4334
Dissolved	3000	4803	9853	9785	8347	4106
Suspended	760	225	175	85	355	228
Volatile	2030	2104	4050	1254	5074	1714
pH	6.7	6.0	6.6	6.8	7.0	5.0
Color (Pt-Co units)	1250	1000	12044	2618	5618	1826
Turbidity	43	3	opaque	0.38	opaque	15
Conductivity (μmho/cm)	2000	3900	9000	9600	5000	4000
Alkalinity	140	456	587	182	341	65
Hardness	32	57	74	135	75	97
Ammonia Nitrogen	24	5	3	3	4	12
Total Kjeldahl Nitrogen	25	11	6	6	10	14
Phosphorus	160	412	15	6	41	3.0
Phenols	1.0	0.40	0.52	0.1	0.1	0.1

TABLE J-1. (continued)

Metal Analyses[a]	#60	#70	#40	#80	#81	#82
Calcium	2.4	4.0	2.1	5.9	3.7	8.5
Chromium	0.13	0.19	8.1	3.1	1.4	-
Copper	0.2	1.2	8.6	0.64	0.66	6.2
Iron	1.3	1.3	10.3	12.0	7.0	2.9
Magnesium	1.0	6.0	12.0	13.0	24.0	-
Manganese	0.53	0.08	0.28	0.43	1.8	0.27
Mercury (µg/ℓ)	-	6.0	-	5.5	6.0	1.0
Nickel	0.33	0.17	1.2	1.9	8.0	0.56
Zinc	2.9	3.4	5.2	5.0	3.0	20.0

[a] Unless otherwise indicated, all units are in mg/ℓ with the exception of pH, which is unitless.

the membrane unit were not monitored. The average value for the feed, based on the concentrate characteristics and the membrane performance, were calculated (Table J-2).

The raw wastewater feed was drawn from the plant composite sewer and was not constant. The calculated values are the characteristic of an average waste stream that would result in the concentrate characteristics that were measured. The values of membrane rejection, used in calculations, were observed for each constituent at each mill.

Concentrate treatability results for six plants located in South Carolina and involved in this study will be discussed in this section. They are Plant #60, Plant #70, Plant #40, Plant #80, Plant #81, and Plant #82. The composite waste concentrate from Plant #40 was mixed on a 60/40 basis with an indigo wash water concentrate obtained from their Plant #40-1 to observe the effect of indigo on the biological as well as chemical treatability of the Plant #40 mixture. The concentrate from Plant #60 was a 50/50 mixture of concentrates from two membranes: cellulose acetate (UOP) and hydrous Zr(IV) oxide-polyacrylate (Selas).

ANALYTICAL PROCEDURES

The following is a brief summary description of the chemical analyses and tests performed during this study. For further description and full detail of the principles, theories, and techniques involved in each test, see Standard Methods for the Examination of Water and Wastewater.[a]

Alkalinity

Alkalinity is defined as the capacity of water to accept protons. It is imparted by the salts of weakly ionized acids and the unionized portion of weakly ionized bases and/or free bases at high pH values. Alkalinity is determined by titration to pH 4.5 with standard sulfuric acid solutions, and is reported in milligrams per liter of sample.

Ammonia Nitrogen

Ammonia nitrogen is the concentration of ammonium and simple amine structures present in a sample, expressed as milligrams nitrogen per liter of sample. Ammonia nitrogen is desirable in biological treatment as a source of nutrient for the microorganism cultures. The level of ammonia nitrogen required for best treatment has been reported to be, in ratio form, ppm BOD:ppm NH_3-N = 100:5. Ammonia nitrogen is measured by the Nessler colorimetric technique, which results in the development of a colored complex whose absorbance is evaluated at 410 nanometers on a Spectronic 20 spectrophotometer.

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[a] 13th Edition, A.P.H.A., 1971.

TABLE J-2. CHARACTERISTICS OF RAW WASTEWATER FEED TO HYPERFILTRATION UNITS[a]

Analyses	Plant #81	Plant #82	Plant #60	Plant #80	Plant #40	Plant #70
COD	925	276	265	541	1687	415
BOD_5	390	89	29	84	166	126
TOC	-	170	97	85	606	215
Alkalinity	39	10	26	38	109	56
Hardness	8	10	4	14	8	6
Total Solids	928	553	390	1331	1315	560
Dissolved Solids	890	524	314	1326	1293	535
Suspended Solids	-	-	-	-	-	-
Volatile Solids	535	211	206	192	457	242
Color	562	187	127	262	1227	50
Turbidity	-	2	-	0.04	-	-
Conductivity	562	492	227	1433	1307	444
Phenol	0.01	0.016	3	0.02	0.06	0.04
Mercury	-	-	-	-	-	-
Manganese	0.38	0.03	0.07	-	-	0.008
Calcium	0.79	0.86	0.58	-	-	0.40
Iron	0.01	0.30	0.41	-	-	-
Nickel	0.17	0.06	0.05	-	-	-
Chromium	0.31	-	-	-	0.86	-
Zinc	0.08	2	-	-	0.56	-
Copper	2	0.02	0.16	-	0.90	-

[a] Calculated from measured membrane performance and concentrate characteristics, Table J-1.

Biochemical Oxygen Demand (BOD)

The BOD represents the organic content of a wastewater sample which is biodegradable under a given set of circumstances, measured as milligrams oxygen for biodegradation per liter of sample. The BOD is measured by determining the change in dissolved oxygen (DO) content over a five-day period of an aliquot of the sample which has been diluted and seeded with a microorganism culture and nutrients and incubated at 20°C. A correlation is often made between BOD and COD, in that BOD represents the portion of the COD which is biodegradable, and the ratio BOD/COD represents the fraction of biodegradability.

Chemical Oxygen Demand (COD)

The COD represents the oxygen required to totally oxidize the organic content of a wastewater sample to carbon dioxide and water, expressed as milligrams oxygen per liter of sample. COD is measured by reacting a desired and known aliquot of wastewater sample with an excess of potassium dichromate in 50% sulfuric acid. After a two-hour reflux, the excess dichromate is titrated with ferrous ammonium sulfate solution to a ferrion endpoint. The basic chemical reaction is the oxidation of organics and the reduction of dichromate to chromic ion.

Color

Color represents a measure of the contamination in a water sample which is visually detectable. Color may be reported as either apparent color, which results from investigating a raw sample, or true color, which results from investigating a filtered sample (the filtration step removes turbidity from colloids and suspended solids). Color is expressed in Platinum-Cobalt units (Pt-Co or PCU). For the analyses performed in this work, apparent color at 410 nanometers on a Spectronic 20 spectrophotometer was found.

Conductivity (Specific Conductance)

Conductivity is the degree to which a liquid sample will conduct an electric current in the presence of an applied electrical potential, expressed as micro-ohms per centimeter. Conductivity gives an indication of the total ionic content of the sample, since the more electrolyte present, the higher the conductivity. Conductivity measurements are made using standard conductance cells and electrical bridges (usually optical or meter null potentiometer bridges) such as Beckman Instruments and Balsbaugh Laboratories bridge and cell systems.

Dissolved Oxygen

The dissolved oxygen is the concentration of oxygen which is dissolved in a water sample, expressed as milligrams oxygen per liter of water. Dissolved oxygen levels in water can range between 0 mg/ℓ and saturation, which is 9.1 mg/ℓ at 20°C. Dissolved oxygen is measured by the membrane polarographic technique, using a conventional analyzer such as the Yellow

Springs Instruments (YSI) Model 54 meter. Changes in dissolved oxygen can often indicate the presence of a biological culture which may be degrading a waste sample. This forms the basis of the BOD test.

Hardness

Hardness refers to the characteristic of water which represents the concentration of calcium and magnesium ions in the water, expressed as milligrams calcium carbonate per liter of sample. Hardness is determined by titrating with a standard EDTA solution to the Eriochrome Black T indicator endpoint.

Metals

The evaluation of the concentrations of individual metals in a wastewater sample is performed using an atomic adsorption spectrophotometer. The samples are first treated with acid to solubilize most metal compounds and the samples are then aspirated into the flame for determination. Comparison of adsorption characteristics of the samples with standards for the desired metals are made, and the metal concentration determined from this.

pH

The pH of a liquid is a measure of its acidity or basicidity, and is defined as the negative base 10 logarithm of hydrogen ion concentration. Measurement of pH is accomplished using a pH meter with standard electrodes.

Phenols

The phenol concentration as defined in this study refers to the concentration of phenol, ortho- and meta- substituted phenols, and some para-substituted phenols in a wastewater sample. These are the phenolic compounds which react with 4-aminoantipyrene solution to yield a gold color, the intensity of which is proportional to the concentration of phenols present. The developed color is evaluated on a Spectronic 20 spectrophotometer at 510 nanometers, and is expressed as milligrams phenol per liter of sample.

Phosphorus

Phosphorus as determined for this study refers to the concentration of ortho-phosphates in a wastewater sample reported as milligrams phosphorus per liter of sample. Phosphorus is measured by the Stannous Chloride Method, which produces a highly colored heteropoly acid, molybdenum blue, the adsorbance of which can be evaluated at 690 nanometers on a Spectronic 20 spectrophotometer.

Dissolved Solids

Dissolved solids represent the concentration of matter in an aqueous sample which passes through Whatman 42 filter paper and becomes solid when the filtrate is dried as in total solids. Dissolved solids is composed of soluble salts and organic compounds, and is expressed as milligrams solid per liter of sample.

Suspended Solids

Suspended solids refers to the concentration of matter in a wastewater sample which is removed by filtering the sample, expressed as milligrams ~~per~~ solids per liter of sample. Suspended solids is measured as the difference between total and dissolved solids. Alternately, a tarred filter may be used to vacuum filter an aliquot of the sample, the filter dried, and ~~reighed~~ weighed. Millipore, Gelman, and Nucleopore Systems are among those commonly used in the latter technique.

Total Solids

Total solids represent the concentration of matter in an aqueous sample which remains when the water is removed, expressed as milligrams solid per liter of sample. Total solids is measured by drying a measured aliquot of sample in a tarred beaker at 105°C for twenty-four hours, cooling, and reweighing the beaker.

Volatile Solids

Volatile solids refer to the concentration of solid matter from a total solids test which volatilizes at 600°C for fifteen minutes, expressed as milligrams solid per liter of sample. To perform volatile solids, a crucible is used instead of a beaker. Total solids is first performed, and then the residue in the crucible is heated for the volatile solids test, cooled, and reweighed. Volatile solids usually represents the majority of the solid organic content of a sample, since the organics are oxidized to carbon dioxide and water at the high temperature used, while most inorganic salts remain.

Total Organic Carbon (TOC)

The concentration of carbon which is organically bound in a wastewater sample is referred to as total organic carbon, and is expressed as milligrams per liter. TOC is determined by first injecting a desired aliquot of the sample into a 950°C column with special packing. All the carbon, whether organic or inorganic, is oxidized to CO_2 which flows into an infrared detection system for measurement. Then inorganic carbon is found by injecting a second aliquot into a 150°C column with packing, in which the inorganic carbon is oxidized to CO_2 and read in the infrared detector. Total organic carbon is then evaluated as the difference between total carbon and inorganic carbon.

Turbidity

Turbidity is defined as that quality of a water sample which causes it to exhibit a cloudy or milky appearance. Turbidity is caused by colloids and finely suspended solids. Measurement of turbidity is made by determining the amount of light which a sample scatters when a light source and a detector are placed ninety degrees apart. Standard turbidity instruments such as the Hach Model 2100 A Turbidimeter may be used with standards, and the results expressed as Formazin Turbidity Units (FTU).

BIOLOGICAL TREATMENT

Theory of Biological Treatment[a]

Biological waste treatment systems are operated on the principle that numerous species of microorganisms are able to consume organic materials in an aqueous system and utilize these nutrients as food. By this process, organics are removed from the water and the microorganisms live and reproduce. If the waste to be treated is of a type that is easily degraded by the microorganism colonies, the waste is said to be biodegradable. If the waste cannot be broken down biologically, or shows considerable resistance to such treatment (as by the presence of toxic metals or chemicals, etc.), it is said to be relatively non-biodegradable.

There are several methods of determining the biodegradability of a waste. Perhaps the simplest is to obtain the COD and BOD_5 and BOD_{30} of the waste, and calculate the BOD to COD percent ratio, or the percent biodegradable as

$$\%\ \text{biodegradable} = \frac{BOD_{30}}{COD} \times 100.$$

A more accurate measure of the biodegradability is obtained from a biological treatability study as described in this section. In such a study, the raw waste, after suitable pH and nutrient adjustments, is fed into a biological oxidation chamber, which is a bench-scale aeration lagoon. This chamber is charged with a biological culture which has been acclimatized to the waste which it is to degrade. Air is bubbled through the chamber since the bioculture requires oxygen to assimilate the food supply in the organics. The reactor effluent is then allowed to become quiescent for a time, which allows the entrained bioculture to settle out and be returned to the reactor. The liquid which remains is the clarified effluent (or decantate) and is the treated sample which is discharged from the biological system either to the environment or to further treatment steps.

There are several methods of determining the degree of treatment being achieved in a biological system. The simplest method is to measure the dissolved oxygen depletion, or the rate at which a mixed sample from the reactor will consume dissolved oxygen. If almost no DO is consumed, it can be assumed that biodegradation is not occurring to a great extent. On the other hand, a significant DO depletion (say, for instance, 1 mg/ℓ DO in two - five minutes) indicates that the system is biodegrading the waste. Measurement of COD and BOD are made throughout the time the system is operated, with decreases in these parameters in the decantate samples over the inlet feed samples indicating the degree of biological treatment. The measurement of settleable solids is also important, since an increase of the floc-like settleable mass of solids in the reactor indicates the conversion of soluble organics into insoluble biomass (insoluble organics plus bacterial sludge).

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[a] Metcalf and Eddy, Inc. Wastewater Engineering, Collection, Treatment and Disposal. McGraw Hill, New York, NY, 1972.

Biological Treatability Study - Experimental Methods

The biological portion of the treatability study was conducted using a batch-fed, fill-and-draw apparatus as shown in Figure J-1. A ten-day retention time was chosen for the study. The container was acclimated using 6 liters of composite concentrate waste plus biological seed.

After acclimation, the daily sampling schedule was started. To counteract evaporating, deionized makeup water was added to the reactor each day. The reactor cross-sectional surface area was approximately 300 cm^2. On a daily basis, 1.0 liter was removed in an Imhoff cone and allowed to settle for one hour. While the 1.0 liter was settling, 0.3 liter of the clarified liquor was removed from the Imhoff cone (including the settled sludge) were returned to the reactor. Then 0.6 liter of feed (the composite concentrate sample described above) was added to the reactor. This procedure, with a net reactor volume of 6 liters and a daily throughput of 0.6 liter resulted in a theoretical retention time in the reactor of ten days. Six daily samples were taken on Monday through Saturday, with no sample taken on Sunday. Samples of the mixed reactor and of the decantate were composited over three-day intervals, giving two mixed reactor samples and two decantate or clarified samples per week.

On approximately day 30 of each study, the reactor was brought to 1000 mg/ℓ of powdered activated carbon and from that time forward, 100 mg/ℓ of carbon were added to the feed each day. This was done to observe whether carbon added to the system would tend to adsorb any component of the waste, thereby effecting better purification of the wastewater in the treatment system.

CHEMICAL TREATMENT WITH ALUM AND CARBON

Theory of Coagulation

Coagulation refers to the unit operation employed in wastewater treatment that invokes the formation of chemical bridges or flocs that adsorb, entrap, or otherwise cause an agglomeration of suspended colloidal matter. Colloidal particles are small particles which can remain suspended in a liquid medium for indefinite periods of time. The stability of colloids is attributed to the fact that they are electrically charged, and thus tend to repel each other in solution. To bring about coagulation this charge effect must be reduced. This is usually achieved by one of three techniques[a]:

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[a] Richard D. Ross. Industrial Waste Disposal. Van Nostrand Reinhold, New York, NY, 1968.

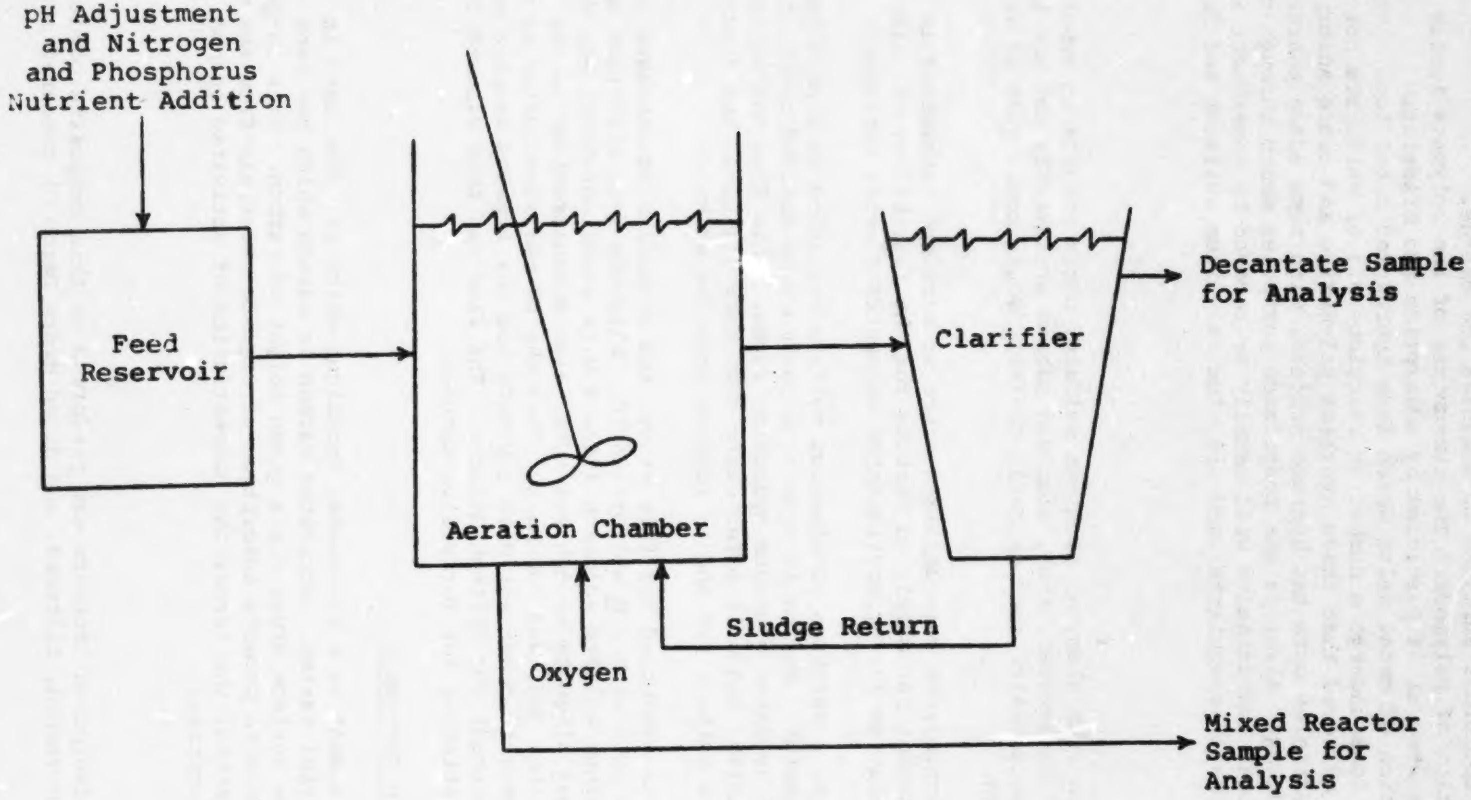
pH Adjustment
and Nitrogen
and Phosphorus
Nutrient Addition
Feed
Reservoir
Aeration Chamber
Oxygen
Clarifier
Sludge Return
Decantate Sample
for Analysis
Mixed Reactor
Sample for
Analysis

Figure J-1. Schematic diagram of a batch fed biological reactor.

(1) Addition of potential-determining ions or electrolytes which can react with the colloidal surfaces to decrease the charge.

(2) Addition of polymers. The sub-unites of the polymers ionize and bring about the removal of particles by adsorption and bridging.

(3) Addition of metal salts which form hydrolyzed metal ions. The hydrated metal ions undergo a number of reactions all of which are not known. However, it is believed that these hydrates polymerize and cause adsorption of colloidal particles onto the hydrate surface, with some added enhancement of polymer bridging. Also, as the coagulated particles sweep through the liquid, additional contaminants will usually be removed by enmeshment in the floc. The two major coagulants used are alum (aluminum sulfate) and ferric chloride.

Alum Tests

Coagulation with alum, or aluminum sulfate, often results in substantial purification of wastewater, thus, alum was chosen arbitrarily for use in this study. Other metal salts such as $FeCl_3$ or $(Fe)_2(SO_4)_3$ could just as well have been chosen.

No polyelectrolytes were utilized since we were not interested in optimizing treatment but merely in testing for the feasibility of using chemical flocculation for hyperfiltration concentrate waste treatment.

In practice, a solution of aluminum sulfate was added to a pH-adjusted sample of wastewater. The pH is then re-adjusted to a desired level, at which a floc of hydrated aluminum hydroxide forms. This floc has substantial adsorptive capacity, and will often carry down many colloidal and dissolved impurities as it settles out and is removed from the solution.

In the tests conducted for this study, the composite concentrate sample was adjusted to pH 5 with 1 N sulfuric acid. Aliquots were withdrawn and sufficient aluminum sulfate solution (from a 0.1% stock solution) was added to the individual aliquots to achieve total alum concentrations in the samples of 50, 100, 300, and 500 mg/ℓ. Then the pH was re-adjusted to 6.0 (maximum floc density observed) with 1 N NaOH and the treated samples were stirred (flocculated) for fifteen minutes. The floc was then allowed to settle with no stirring for forty-five minutes.

Theory of Carbon Treatment

Carbon treatment is a wastewater technique which is often used in treating industrial wastes. Activated carbon is carbon which has been treated to form large surface areas for a given weight of carbon. This large surface area tends to promote adsorption of organic materials from the water. As would be expected, the larger the concentration of activated carbon, the greater the adsorption.

Carbon Study

A carbon adsorption isotherm was performed on this composite concentrate waste using (pre-washed, filtered, and dried Hydro Darco C) powdered activated carbon. Aliquots (20°C) of the composite concentrate wastes were placed in beakers under a gang stirrer. Sufficient powdered activated carbon (accurately weighed) was added to the individual beakers to achieve concentrations of carbon in the samples of 500, 2500, and 5000 mg/ℓ. The samples, along with a blank to which no carbon was added, were stirred under the gang stirrer for one hour, and then filtered through two circles of Whatman Number 42 filter paper (0.6µ).

DISCUSSION

Biological Treatability

As a general rule[a], it has been found empirically that the ratio of BOD_5 to nitrogen to phosphorus in a textile wastewater should be approximately 100:5:1, respectively, in order to provide sufficient nutrients for the biodegradation of wastes in an aerated lagoon. Consequently, the BOD_5, ammonia nitrogen, and phosphorus content of each concentrate sample was determined during the initial acclimation stage of each study to allow time for any nutrient additions to the feed concentrate that might be necessary before the actual sampling schedule was started.

The normalized (based on BOD_5 as 100) average nutrient ratio for the concentrates as received in the laboratory (before the study) was 100:30:10. Plant #81, Plant #70, and Plant #82 had low phosphorus concentrations (100:1:1) with Plant #40 and Plant #80 exhibiting sufficient ratios (approximately 100:9:1) and Plant #60 concentrate showing a high ratio (100:150:60).

Phosphorus addition was accomplished for the deficient Plant #81, Plant #70, and Plant #82 samples by adding the required amount of Na_2HPO_4 (pH adjusted) to the concentrate feed samples.

The overall BOD_5 ranges for the nutrients present in the concentrate samples varied from a low of 270 mg/ℓ to a high of 3745 mg/ℓ (see Table J-1). Nitrogen concentrations varied from 3 mg/ℓ to 24 mg/ℓ and phosphorus varied from 3 mg/ℓ to 160 mg/ℓ.

The Plant #81 concentrate required fairly constant day-to-day addition of 1 N HCl (equivalent to 36 kg of concentrated HCl per cubic meter of concentrate, overall) to keep the pH from constantly rising throughout the study. This was considered to be an unusual problem since CO_2 in the system as a by-product of the biodegradation process would be expected to lower the pH (due to carbonic acid buildup) rather than raise it. Apparently, some basic by-product was constantly produced during the biodegradation of Plant #81's concentrate.

The overall average ammonia nitrogen removal during the studies (from acclimation to shutdown) was 3.8% with Plant #70 exhibiting the lowest removal (-38%) and Plant #60 showing the highest removal (93.3%).

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[a] Eckenfelder, W. W., and D. J. O'Connor. Biological Waste Treatment. Pergammon Press, New York, NY, 1961.

As previously mentioned, the BOD_{30}/COD ratio or percent biodegradability can sometimes furnish insight into the feasibility of biological treatability. The overall average percent biodegradability for the six mills was 40% with Plant #80 showing the lowest percentage (18%) and Plant #70 giving the highest percentage (59%). The values of this ratio correspond fairly well with the actual biological treatability results for each mill obtained through this study.

The dissolved oxygen (DO) content in the samples was monitored daily. The DO data is extremely important since the oxygen demand for an aerated lagoon is considered in determining the aeration and total aerator horsepower requirements. The overall average DO uptake was 46 mg/ℓ/hr at the beginning of the study; 21 mg/ℓ/hr was the lowest value observed (Plant #60) and 120 mg/ℓ/hr was the highest value observed (Plant #81). At the end of the study, the overall average DO uptake was 8.0 mg/ℓ/hr with 3.0 mg/ℓ/hr being the highest observed uptake (Plant #40). The average DO uptake was consistently observed to be greater at the beginning of a study than at the end. This was attributed to the fact that the bacteria were experiencing exponential growth (therefore requiring more oxygen) at the beginning of a study as well as the fact that the concentration of biodegradable organics present in the concentrate feed was greater at the beginning of a study than at the end.

Settleable solids, measured on a daily basis throughout each study, exhibited an average overall settling rate (all mills) of 38 mℓ/ℓ/hr (0.9 gallon/100 gallons waste/day).

Chemical Treatability

Alum--

Treatment with alum was essentially ineffective up to 500 mg/ℓ with the average COD removal being only 32.2%. The overall average BOD_5 removal was 27.3% and the average color removal was only 33%.

Carbon--

Treatment with activated powdered carbon at the 5000 mg/ℓ level exhibited the same average percent removal of BOD_5 and COD as did alum treatment at 500 mg/ℓ. Carbon removed twice as much apparent color (66.6%) as alum, as would be expected.

Comparison of Treatment Methods

Table J-3 provides an overall picture of the effectiveness of the treatment methods utilized in this study (Biological vs Chemical Treatment) in treating the hyperfiltration wastewater concentrates from the six textile mills studied.

For the biological study, carbon addition to the reactor seemed to have little effect on decreasing the COD or BOD_5, although there was a significant overall average (all mills) increase in the percent apparent color removal (from 19.7% before carbon to an average 30.5% removal after carbon

TABLE J-3. A SUMMARY OF OVERALL BEST RESULTS FOR TREATMENT METHODS

	Percent Removal					
Plant	#60	#70	#40	#80	#81	#82
Biological Study[a]						
BOD_5	86	89	39	95	98	97
COD	44	60	29	83	65	64
Color[b]	16	0	0	27	75	0
Biological Study with Carbon Added						
BOD_5	97	92	36	99	99	95
COD	72	63	35	88	66	63
Color[b]	56	0	0	51	76	0
Alum Treatment[c]						
BOD_5	9	27	14	60	15	38
COD	10	23	23	78	14	45
Color[b]	0	9	0	76	48	65
Powdered Activated Carbon[d]						
BOD_5	61	29	76	72	35	23
COD	73	19	69	60	32	52
Color[b]	62	67	67	71	80	53

[a] Percent removal based on the results for the entire period including time before and after 1000 mg/ℓ carbon addition. Removal based on decantate sample compared to the raw reactor feed.

[b] Unfiltered or "apparent" color.

[c] Data for the alum treatment based on the best treatment, 500 mg/ℓ in all cases. Removal based on decanted sample after floc settling compared with the feed.

[d] Data for the carbon treatment based on the best overall treatment, 5000 mg/ℓ in all cases. Removal based on a treated filtered sample compared with the untreated filtered raw feed.

addition). Carbon had no measureable effect in removing apparent color from the Plant #70, Plant #40, and Plant #82 concentrate samples.

Alum treatment was ineffective exhibiting an overall 27.2% removal of BOD_5 with Plant #60 exhibiting the least BOD_5 removal (9.2%) and Plant #80 giving the best treatment (60% removal). An overall average of only 32.2% of the COD was removed by alum treatment with results ranging from 9.6% for Plant #60 to 78% for Plant #80. The overall average color removal was 33% using alum with results ranging from 0% for Plant #60 and Plant #40 to 76% for Plant #80.

Carbon treatment was not very successful with the overall average BOD_5 removal being 49.4% with results ranging from 22.7% for Plant #82 to 76.1% for Plant #40. The overall average COD removal using carbon was 50.6% with results ranging from 18.7% at Plant #70 to 72.7% at Plant #60. The color removal using carbon was acceptable considering the fact that a concentrate waste was being treated. The overall average color removal was 66.6% with results varying from 52.7% at Plant #82 to 79.8% at Plant #81.

CONCLUSIONS

From the descriptions and data presented in this section, it appears that:

(1) Hyperfiltration produces a concentrated wastewater which can be treated by conventional waste treatment techniques.

(2) Long-term biological treatment is a feasible technique for treating the concentrate from hyperfiltration.

(3) Addition of powdered activated carbon to the concentrate during biological treatment is of limited utility in decreasing total organics in both the mixed reactor and decantate samples, but can significantly reduce color.

(4) Alum in concentrations up to 500 mg/ℓ is ineffective in decreasing the organic loading or physical color of the concentrate.

(5) The addition of powdered activated carbon to the concentrate samples (as a chemical treatment method and not as an adjunct to biological treatment) was relatively ineffective in lowering organic loading yet did remove significant amounts of color. The degree of color removal was shown to increase as the concentration of carbon was increased up to and including 5000 mg/ℓ.